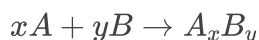


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Mole concept

Stoichiometry is a branch of chemistry which deals with quantitative relationships of the reactants and products in a chemical reaction. The quantity of substance involved in measurement has different states (solid, liquid and gas) and forms (mixture and compound).

The stoichiometry calculations are basically arithmetic calculations, but confounded by scores of measuring terminologies. These terms are required to represent atomic or molecular level of association involved in chemical reactions. Besides chemical substance reacts or combines in definite proportion which we account by valence factor. Corresponding to valence factor, there are measurements which measures the proportion in which one element or group of elements reacts or combines with another element or group of elements.



A good part of stoichiometry is about mastering measuring terms. In this module, we seek to have a clear idea of mole and associated concept which is central to stoichiometry calculation.

Moles

Moles measure quantity of substance. There is a subtle ambiguity about treating “moles” – whether as “mass” or “number”. We take the position that it measures “amount of substance”, which can be either be expressed in terms of mass or in terms of numbers. The two approaches are equivalent and need not be a source of ambiguity any further. We only need to interpret the meaning as appropriate in a particular context.

One mole is defined as N_o entities of the substance, where N_o is equal to Avogadro's number. N_o is generally taken as 6.022×10^{23} . If need be, then we may use still closer approximation of this number.

Relation between Mole and Molecular weight

The mole and molecular weight are designed to be related. Argument goes like this :

1: Molecular weight is arithmetic sum of atomic weights of constituent atoms.

2: Atomic weight is expressed in “atomic mass unit (a.m.u)”.

3: The atomic mass unit is the mass of $\frac{1}{12}$ th of C-12 atom. This is average weight of constituent 6 protons and 6 neutrons forming nucleus of C-12 atom. The a.m.u, therefore, is close to the mass of either a single proton or single neutron as a constituent of C-12. The a.m.u is numerically equal to :

$$1a.m.u = 1.66 \times 10^{-27} \text{ kg} = 1.66 \times 10^{-24} \text{ gm}$$

4: On the scale of a.m.u, the atomic weight of a carbon atom is exactly “12” and that of hydrogen is “1.008” or about “1”.

5: The number of C-12 atoms present in the quantity expressed in grams but numerically equal to atomic weight (as measured in a.m.u.) is given as :

$$N_o = \frac{\text{grams numerically equal to atomic weight}}{\text{Mass of one C-12 atom in gram}} = \frac{12}{12 \times 1.66 \times 10^{-24}}$$

The important point about this ratio is that “12” as atomic weight in the numerator and “12” as the number of a.m.u units in a single atom of C-12 cancels out, leaving us with a constant ratio :

$$\Rightarrow N_o = \frac{1}{1.66 \times 10^{-24}} = 6.022 \times 10^{23}$$

Clearly, this ratio is same for all elements. It means that the numbers of atoms in the grams numerically equal to atomic weight is N_o for all elements. Putting it equivalently, the mass of a collection N_o atoms of an element is equal to grams numerically equal to atomic weight.

6: We conclude that quantity in grams numerically equal to atomic weight contains N_o number of a particular element. This provides us with another definition of mole. In the case of an element, a mole of an atom means N_o numbers of that atom having mass in grams numerically equal to atomic weight. Important to note here is that term like "mole or moles of atoms" is a valid term. It can be emphasized that the term mole appears to be connected to molecules only, but actually it is a general concept which determines quantity of substance - atoms/molecules/ions/entities.

7: Extending the concept to molecule, a mole means N_o numbers of molecules having mass in grams numerically equal to molecular weight.

8: Further extending the concept in general, a mole of identical entities means N_o numbers of that entity having mass equal to N_o times mass of one entity.

The official SI definition of mole is :

Mole

The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

Gram moles (n)

This term emphasizes the mass aspect of mole. One “gram mole” expresses mass of N_o elements, molecules, ions (as the case be) in grams. It is equal to mass in grams numerically equal to molecular weight.

If the mass of a chemical entity is “g” grams, then the given mass contains “n” gram-moles of the entity :

$$\text{gram moles}(n) = \frac{\text{Mass in gram}}{\text{Molecular weight}} = \frac{g}{M_o}$$

The gram mole or simply mole in the given grams of a sample means that there are “n” moles of substance present. This formula is widely used to express grams of substance in terms of gram moles and vice-versa.

Note that we use symbol M_o to denote molecular weight as we reserve the symbol “M” to denote molarity in the study of stoichiometry.

Gram atoms

It is a special case of gram moles in which chemical entity is an element. In this case, “gram atoms” substitutes “gram moles” and “atomic weight” replaces “molecular weight”.

$$\text{gram-atoms}(n_a) = \frac{\text{Mass in gram}}{\text{Atomic weight}} = \frac{g}{A}$$

The atomic and molecular weights of oxygen (O_2) are 16 and 32 respectively. If we consider a sample of 32 grams of oxygen, then

$$\text{gram moles}(n) = \frac{g}{M_o} = \frac{32}{32} = 1$$

Clearly, there are No molecules in the given 32 grams of oxygen sample. On the other hand, gram-atoms is :

$$\text{gram-atoms}(n_a) = \frac{g}{A} = \frac{32}{16} = 2$$

Thus, there are $2N_o$ atoms of oxygen in the given 32 grams of oxygen sample. These results are consistent with our understanding of the constitution of diatomic oxygen gas. The important point to keep in mind is that we need to employ the concept of “gram- atoms (g-atoms)” to elements only irrespective of whether it is mono-atomic or polyatomic.

Example:

Problem : What is mass of one molecule of Calcium carbonate?

Solution : The mass of one molecule of Calcium carbonate is equal to its molecular weight (M_o)

$$m = M_o = 40 + 12 + 16 \times 3 = 100 \quad a.m.u = 100 \times 1.66 \times 10^{-24} \quad gm = 1.66 \times 10^{-22} \quad gm$$

Example:

Problem : What is mass of one mole of Calcium carbonate?

Solution : The mass of one mole of Calcium carbonate is equal to grams numerically equal to molecular weight (M_o)

$$m = M_o \text{ gm} = (40 + 12 + 16 \times 3) \text{ gm} = 100 \text{ gm}$$

Example:

Problem : Find the number of moles in 500 grams of pure Calcium carbonate?

Solution : The numbers of moles is given by :

$$n = \frac{g}{M_o} = \frac{500}{100} = 5$$

Example:

Problem : Which represents greatest mass among 100 gm of calcium, 3 g-atoms of calcium , 1 mole of calcium oxide, 10^{25} molecules of oxygen?

Solution : We convert each of the given quantity in grams for comparison :

$$100 \text{ gm of calcium} = 100 \text{ gm}$$

$$3g - \text{atoms of calcium} = 3 \times A_{Ca} = 3 \times 40 = 120 \text{ gm}$$

$$1 \text{ mole of calcium oxide} = M_{CaO} \text{ gm} = 40 + 16 = 56 \text{ gm}$$

$$10^{25} \text{ molecules of oxygen} = \frac{10^{25}}{6.022 \times 10^{23}} \text{ moles} = 0.166 \times 10^2 \text{ moles}$$

$$\Rightarrow 10^{25} \text{ molecules of oxygen} = 16.6 \text{ moles} = 16.6 \times M_{O_2} \text{ gm} = 16.6 \times 32 = 531.2 \text{ gm}$$

Clearly, 10^{25} molecules of oxygen represents greatest mass.

Number of entities

The number of moles in a given mass of a molecule is given by :

$$\text{moles}(n) = \frac{g}{M_o}$$

Since each mole has N_o entities, the total numbers of entities in “n” moles is :

$$\text{Total number of molecules}(N) = nN_o = \frac{g}{M_o} \times N_o$$

If we are interested to count atoms in a sample of an element, then we use “gram atom” as :

$$\text{Total number of atoms}(N) = n_a N_0 = \frac{g}{A} X N_0$$

Example:

Problem : If 10^{22} water molecules are removed from 100 mg of water, then find the remaining mass of water.

Solution : Here we need to find the mass of 10^{22} water molecules. We know that numbers of molecules is related to mass in gram as :

$$N = n N_0 = \frac{g}{M_o} X N_0$$

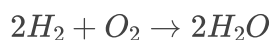
$$\Rightarrow g = \frac{N M_o}{N_0} = \frac{10^{22} X 18}{6.022 X 10^{23}} = 2.989 X 0.1 = 0.2989 \text{ gm} = 2.989 \text{ mg}$$

$$\Rightarrow \text{remaining mass of water} = 100 - 2.989 = 97.011 \text{ mg}$$

Mole concept

Chemical reactions involve dissociation and association at atomic/molecular/ionic level. The measurements of constituent entities of a reaction can be carried out using conventional mass measurements in grams or kilograms. What is the need to carry out analysis in terms of moles?

Let us have a look at the chemical reaction :



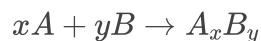
Let us further consider that there are 2 gms of hydrogen involved in the reaction. Can we interpret the given balanced equation to predict the mass of oxygen involved in the reaction? Clearly, it would not be possible unless we know the molecular mass. In terms of molecular mass, we see that 4 a.m.u of hydrogen reacts with 32 a.m.u of oxygen. This mass correlation, however, is slightly incomprehensible to our measurement sense as a.m.u is very minute mass almost incomprehensibly too small for our perceptible laboratory measurements in grams.

We can though extend the molecular mass proportion to grams. We note that the mass ratio of two elements in the reaction is 4:32 i.e. 1:8. Hence, 2 grams of hydrogen reacts with 16 grams of oxygen. This completes the picture. But, slight discomfort is that the correspondence of mass is not directly related with the numbers of molecules (coefficients of balanced chemical equation) involved in the reaction.

Mole concept simplifies the mass relation among reactants and products such that we can base our calculation on the coefficients (numbers of molecules involved in the reaction). At the same time, mass or the quantity of substance is on lab scale in grams. Looking at the equation, we can say that 2 molecules of hydrogen react with one molecule of oxygen. Extending this understanding of

reaction to the moles of the substance, we come to the conclusion that “2 moles of hydrogen reacts with 1 mole of oxygen”. Here, we have simply scaled the molecular relation N_o times.

For a general reaction of the type :



We say that “x moles of A reacts with y moles of B”.

This is a very powerful deduction popularly known as “mole concept”. It connects the measurement of mass neatly with the coefficients which are whole numbers. Further as moles are connected to mass in grams, measurement of quantities can be easily calculated in practical mass units like grams.

Example:

Problem : Find the mass of KCl and oxygen liberated when 24.5 grams of $KClO_3$ is heated. Assume 100 % decomposition on heating. Given, $M_K = 39$.

Solution : On heating $KClO_3$ decomposes as :



In order to apply mole concept, we need to find the moles of $KClO_3$ in the sample.

$$\text{moles of } KClO_3 = \frac{24.5}{\text{molecular wt of } KClO_3}$$

Here, molecular weight of $KClO_3$ is :

$$\text{molecular wt of } KClO_3 = 39 + 35.5 + 3 \times 16 = 122.5$$

Putting this value in the equation of moles :

$$\Rightarrow \text{moles of } KClO_3 = \frac{24.5}{\text{molecular wt of } KClO_3} = \frac{24.5}{122.5} = 0.2$$

Applying mole concept to the equation, we have :

$$2 \text{ mole of } KClO_3 \quad \equiv \quad 2 \text{ moles of } KCl \quad \equiv \quad 3 \text{ moles of oxygen}$$

$$1 \text{ mole of } KClO_3 \quad \equiv \quad 1 \text{ moles of } KCl \quad \equiv \quad \frac{3}{2} \text{ moles of oxygen}$$

$$0.2 \text{ mole of } KClO_3 \quad \equiv \quad 0.2 \text{ moles of } KCl \quad \equiv \quad \frac{0.6}{2} \text{ moles of oxygen}$$

At this point, we need to convert the mass measurement from mole to grams,

$$m_{KCl} = n_{KCl} \times M_{KCl} = 0.2 \times (39 + 35.5) = 0.2 \times 74.5 \text{ gm} = 14.9 \text{ gm}$$

$$m_{O_2} = n_{O_2} \times M_{O_2} = \frac{0.6}{2} \times 32 = 0.6 \times 16 \text{ gm} = 9.6 \text{ gm}$$

Ideal gas and mole concept

The concept of mole is applicable to identical entities (atoms, molecules, ions). Thus, its direct application is restricted to pure substances – irrespective of its state (solid, liquid and gas). For all practical purposes, we treat mole as an alternative expression of mass. They are connected to each other via molecular weight for a given pure substance. However, measurement of gas is generally reported in terms of volume in stoichiometric calculation. We would, therefore, need to convert the volume of the gas to mass/mole.

If the gas in question is ideal gas, then we can easily connect volume to mole directly. Ideal gas presents a special situation. The collisions are perfectly elastic and there is no intermolecular force between molecules. The volume occupied by gas molecules is negligible with respect to the volume of ideal gas. It means that the size of molecule has no consequence as far as the volume of ideal gas is concerned. These negligibly small molecules, however, exchange momentum and kinetic energy through perfectly elastic collisions. Clearly, volume depends solely on the numbers of molecules present – not on the mass or size of molecules. This understanding leads to Avogadro's hypothesis :

All ideal gases occupy same volume at a given temperature and pressure. One mole of ideal gas occupies 22.4 litres i.e. 22,400 ml at standard temperature (273 K) and pressure (1 atmosphere) condition.

The gas volume for 1 mole is known as molar volume. The Avogadro's hypothesis provides an important relation between volume and moles of gas present. This relationship does not hold for real gas. But we are served well in our calculation by approximating real gas as ideal gas. The real gas like hydrogen, oxygen etc. may still be close to the ideal gas molar volume at normal temperature and pressure conditions.

Example:

Problem : Air contains 22.4 % oxygen. How many moles of oxygen atoms are there in 1 litre of air at standard condition ?

Solution : The volume of oxygen is 0.224 litre. We know that 22.4 litres contains 1 mole of oxygen molecules. Hence, 0.21 litres contains “n” moles given by :

$$n = \frac{0.224}{22.4} = 0.01 \text{ moles of oxygen molecules}$$

We know that one molecule of oxygen contains 2 atoms. Therefore, numbers of moles of oxygen atoms is 0.02 moles.

Example:

Problem : Calculate the numbers of molecules in 300 cc of oxygen at 27° C and 740 mm pressure.

Solution : We first need to convert the given volume at given temperature and pressure to that at standard temperature and pressure condition. Applying gas law,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$
$$\Rightarrow V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{740 \times 300 \times 273}{760 \times 300} = 265.82 \text{ cc}$$

Number of molecules of oxygen is :

$$\Rightarrow N = \frac{265.82 \times 6.022 \times 10^{23}}{22400} = 7.146 \times 10^{21}$$

Analysis techniques

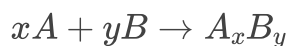
Stoichiometric analysis is about analyzing mass of different chemical species or concentrations of solutions involved in chemical reactions. We employ varieties of different concepts and hypotheses. These principles are primarily based on molecular association of various chemical species in chemical reactions. Most important among these are mole, equivalent weight and gram equivalent weight concepts. Each of these concepts relates amount of different species in chemical reaction in alternative ways. It means that these concepts have contextual superiority over others (suitability in a particular context), but are essentially equivalent.

Stoichiometric analysis is broadly classified as gravimetric or volumetric analysis depending on whether calculations are mass based (gravimetric) or concentration of solution based (volumetric). There is no strict division between two approaches as we encounter reactions which require considerations of both aspects i.e. mass of species and concentration of solution.

In general, gravimetric analysis covers displacement reactions, action of acid on metals, calculations based on balanced equations, decomposition reaction etc. On the other hand, volumetric analysis covers wide ambit of titration including neutralization and redox reactions. Many of the chemical reactions, however, need combination of two analytical approaches. For example, a sequence of chemical process may involve decomposition (gravimetric analysis) and titration (volumetric analysis).

Analyzing chemical equations

Application of mole concept requires a balanced chemical equation. The different constituents of the reaction – reactants and products – bear a simple whole number proportion same as the proportion of the coefficients associated with constituents. According to mole concept, the molar mass of constituents participates in this proportion. For a generic consideration as given :



Here, 1 mole of compound ($A_x B_y$) involves x mole of A and y mole of B. Using symbols :

$$x \text{ moles of A} \equiv y \text{ moles of B} \equiv 1 \text{ mole of } A_x B_y$$

The point to emphasize here is that this is a relation, which is connected by "equivalence sign (\equiv)" - not by "equal to ($=$)" sign. We know that 2 moles of hydrogen reacts with 1 mole of oxygen to form 2 moles of water. Clearly, we can not equate like $2=1=2$. We need to apply unitary method to interpret this relation of equivalence. We say that since x moles of A react with y moles of B. Hence, 1 mole of A reacts with y/x moles of "B". Similarly, 1 mole of B reacts with x/y moles of "A". Once we know the correspondence for 1 mole, we can find correspondence for any other value of participating moles of either A or B.

Mass of participating entities in a reaction

Mole concept is used to calculate mass of individual constituent of a chemical reaction. The proportion of molar mass is converted to determine proportion of mass in which entities are involved in a reaction. The symbolic mass relation for the chemical reaction as given above is :

$$x M_A \text{ gm of A} \equiv y M_B \text{ gm of B} \equiv M_{A_x B_y} \text{ gm of } A_x B_y$$

We apply unitary method on the mass relation related with equivalent sign (\equiv) to determine mass of different entities of the reaction.

Example:

Problem : Calculate mass of lime (CaO) that can be prepared by heating 500 kg of 90 % pure limestone ($CaCO_3$).

Solution : Purity of $CaCO_3$ is 90 %. Hence,

$$\text{Mass of } CaCO_3 = 0.9 \times 500 = 450 \text{ kg}$$

The chemical reaction involved here is :



Applying mole concept :

$$\Rightarrow 1 \text{ mole of } CaCO_3 \equiv 1 \text{ mole of } CaO$$

$$\Rightarrow (40 + 12 + 3 \times 16) \text{ gm of } CaCO_3 \equiv (40 + 16) \text{ gm of } CaO$$

$$\Rightarrow 100 \text{ gm of } CaCO_3 \equiv 56 \text{ gm of } CaO$$

$$\Rightarrow 100 \text{ kg of } CaCO_3 \equiv 56 \text{ kg of } CaO$$

Applying unitary method :

$$\Rightarrow \text{mass of } CaO \text{ produced} = \frac{56 \times 450}{100} = 252 \text{ kg}$$

Example:

Problem : Igniting MnO_2 converts it quantitatively to Mn_3O_4 . A sample of pyrolusite contains 80% MnO_2 , 15 % SiO_2 and 5 % water. The sample is ignited in air to constant weight. What is the percentage of manganese in the ignited sample ? ($A_{Mn} = 55$)

Solution : The sample contains three components. Since this question involves percentage, we shall consider a sample of 100 gm. Water component weighing 5 gm evaporates on ignition. SiO_2 weighing 15 gm does not change. On the other hand, 80 gm of MnO_2 converts as :



Applying mole concept,

$$3 \text{ moles of } MnO_2 \equiv 1 \text{ mole of } Mn_3O_4$$

$$3 \times (55 + 2 \times 16) \text{ gm of } MnO_2 \equiv 1 \times (3 \times 55 + 4 \times 16) \text{ gm of } Mn_3O_4$$

$$261 \text{ gm of } MnO_2 \equiv 229 \text{ gm of } Mn_3O_4$$

Since sample is ignited in air to constant weight, it means that all of MnO_2 in the sample is converted. Using unitary method, we determine mass of converted mass of Mn_3O_4 for 80 gm of MnO_2 :

$$\text{Mass of } Mn_3O_4 \text{ on conversion} = \frac{229}{261} \times 80 = 70.2 \text{ gm}$$

We are required to find the percentage of Mn in the ignited sample. Thus, we need to determine the mass of the ignited sample. The ignited sample contains 70.2 gm of Mn_3O_4 and 15 gm of SiO_2 . Total mass of ignited sample is $70.2 + 15 = 85.4$ gm. On the other hand, amount of Mn in Mn_3O_4 is calculated from its molecular constitution :

$$229 \text{ gm of } Mn_3O_4 \equiv 3 \times 55 \text{ gm of Mn} \equiv 165 \text{ gm of Mn}$$

$$\text{Amount of Mn in 70.2 gm of } Mn_3O_4 = \frac{165}{229} \times 70.2 = 0.72 \times 70.2 = 50.54 \text{ gm}$$

Clearly, 85.4 gm of ignited sample contains 50.54 gm of Mn. Hence,

$$\text{Percentage amount of manganese in the ignited sample} = \frac{50.54}{85.4} \times 100 = 59.2\%$$

Reaction involving gas

In analyzing chemical reaction involving gas, we make the assumption that gases are ideal gases. In general, there are three different situations in which we may use gas volume in chemical analysis :

- Gas volumes are given at STP.
- Gas volumes are given at other temperature and pressure condition.
- Only gas volumes are involved in calculation

In certain situation, reaction involving gas enables us to use gas volumes itself (not the moles) to analyze the reaction. We can extend the concept of molar proportions to volume proportions directly. Such is the case, when only gas volumes are involved in the calculation.

Gas volumes are given at STP

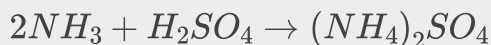
For analyzing gas volumes at STP, we make use of Avogadro's hypothesis. A volume of 22.4 litres of ideal gas contains 1 mole of gas. The number of moles present in a volume "V" at STP is :

$$n = \frac{V}{22.4}$$

Example:

Problem : Determine the amount of concentrated H_2SO_4 required to neutralize 20 litres of ammonia gas at STP.

Solution : The chemical reaction involved is :



Applying mole concept :

$$2 \text{ moles of } NH_3 \equiv 1 \text{ mole of } H_2SO_4$$

$$2 \times 22.4 \text{ litres of } NH_3 \equiv 98 \text{ gm of } H_2SO_4$$

$$\text{Amount of } H_2SO_4 \text{ for 20 litres of } NH_3 = \frac{98}{44.8} \times 20 = 43.8 \text{ gm}$$

Gas volumes are given at other temperature and pressure condition

Under this condition, we first need to convert gas volumes to volumes at STP. We make use of ideal gas law,

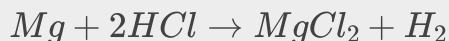
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

We may specify one of the suffix like “1” to represent the given condition and suffix “2” to represent the STP condition.

Example:

Problem : Determine the amount of magnesium required to liberate 900 cc of hydrogen from a solution of HCl at 27°C and 740 mm of Hg. $A_{Mg} = 24$.

Solution : The chemical reaction involved is :



Applying mole concept :

1 mole of Mg \equiv 1 mole of H_2

24 gm of Mg \equiv 22400 cc of H_2 at STP

Using ideal gas law,

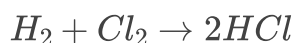
$$\Rightarrow V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{740 \times 900 \times 273}{760 \times 300} = 797 \text{ cc}$$

Using this data to mole relation,

$$\text{Amount of Mg} = \frac{24 \times 797}{22400} = 0.85 \text{ gm}$$

Only gas volumes are involved in calculation

In this case, we are required to consider volumes of gases only. What it means that there is no solid or liquid elements involved in calculation. The reaction may involve solid or liquid components but they are not involved in calculation. In such situation, we can connect volumes of gas components of the reaction directly. Consider the reaction :



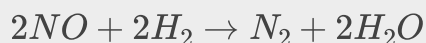
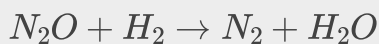
x litres of $H_2 \equiv$ x litres of $Cl_2 \equiv$ 2x litres of HCl

This direct relation is deducted from mole concept under two assumptions (i) all gases are ideal and (ii) temperature and pressure conditions are same for measuring all gases. Under these assumptions, equal numbers of moles of ideal gases occupy same volume. Hence, we can correlate volumes directly as above.

Example:

Problem : A 60 cc mixture of N_2O and NO is mixed with excess H_2 and the resulting mixture of gas is exploded. The resulting mixture contains 38 cc of N_2 . Determine the volume composition of the original mixture.

Solution : The chemical reactions involved are :



Let volume of N_2O be x in the original mixture. Hence, volume of NO in the sample is $60 - x$. Now, the corresponding mole relations are :

$$x \text{ cc of } N_2O \equiv x \text{ cc of } N_2$$

$$(60-x) \text{ cc of } N_2O \equiv \frac{(60-x)}{2} \text{ cc of } N_2$$

According to question,

$$x + \frac{60-x}{2} = 38$$

$$x + 60 = 76$$

$$\Rightarrow \text{Volume of } N_2O = x = 16 \text{ cc}$$

$$\Rightarrow \text{Volume of NO} = 60 - x = 60 - 16 = 44 \text{ cc}$$

Limiting reactant

The participating mass of the reactants may not be exactly same as required by balanced chemical reaction. The reactant which limits the progress of reaction is called limiting reactant (reagent). If g_A and g_B be the mass of two reactants, then moles present are :

$$n_A = \frac{g_A}{M_A}$$

$$n_B = \frac{g_B}{M_B}$$

According to mole concept :

$$x \text{ moles of A} \equiv y \text{ moles of B}$$

$$n_A \text{ moles of A} \equiv \frac{yn_A}{x} \text{ moles of B}$$

For reaction to complete as the limiting case,

$$\frac{yn_A}{x} = n_B$$

$$yn_A = xn_B$$

For A to be limiting,

$$n_B > \frac{yn_A}{x}$$

$$yn_A < xn_B$$

For B to be limiting,

$$n_B < \frac{yn_A}{x}$$

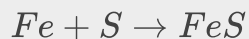
$$xn_B < yn_A$$

$$yn_A > xn_B$$

Example:

Problem : Equal amounts of iron and sulphur are heated together to form FeS. What fraction of iron or Sulphur are converted into FeS. Here, $A_{Fe} = 56$ and $A_S = 32$.

Solution : The chemical reaction involved in the conversion is :



1 mole of Fe \equiv 1 moles of S

Here, $x=y=1$. Now, equal amounts are used. Let “g” gm of each takes part in the reaction. The numbers of moles corresponding to “g” gm are :

$$n_{Fe} = \frac{g}{56}$$

and

$$yn_{Fe} = \frac{g}{56}$$

Similarly,

$$xn_S = \frac{g}{32}$$

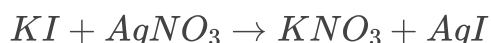
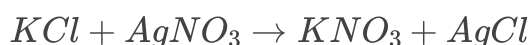
Here, $yn_{Fe} < xn_S$. It means that iron is in short supply and is the limiting reactant. Clearly, all iron is converted into FeS. Hence, fraction of iron used is 1. On the other hand, the moles of Sulphur converted are $\frac{x}{56}$ only as reaction is limited by iron.

$$\Rightarrow \text{Mass of Sulphur converted in the reaction} = \frac{x}{56} \times M_S = \frac{32x}{56}$$

$$\Rightarrow \text{Fraction of sulphur converted} = 32x/56x = \frac{32}{56} = 0.571$$

Multiple reactions

Some chemical reaction under analysis involves simultaneous or concurrent reactions. Consider the example in which a mixture of KCl and KI are treated with excess of silver nitrate ($AgNO_3$) :



We apply mole concept to two concurrent reactions as :

$$1 \text{ mole of } KCl \equiv 1 \text{ mole of } AgNO_3 \equiv 1 \text{ mole of } KNO_3 \equiv 1 \text{ mole of } AgCl$$

and

$$1 \text{ mole of } KI \equiv 1 \text{ mole of } AgNO_3 \equiv 1 \text{ mole of } KNO_3 \equiv 1 \text{ mole of } AgI$$

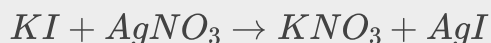
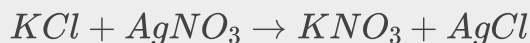
Example:

Problem : 2.2 g of a mixture of KCl and KI yields 3.8 gm of AgCl and AgI, when treated with excess silver nitrate ($AgNO_3$). Find the mass of KCl and KI in the original mixture.

Solution : Since the mixture is treated with excess silver nitrate, both chloride and iodide are completely consumed, forming silver chloride and iodide. Let the initial mixture contains x and y grams of KCl and KI respectively. Then, according to question :

$$x + y = 2.2$$

This is first of two linear equations, which will be used to determine x and y. Now, chemical reactions are :



The amount of AgCl and AgI produced is 3.8 gm. Applying mole concept to first equation,

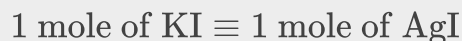


$$\frac{x}{(39 + 35.5)} \text{ moles of KCl} \equiv \frac{x}{(39 + 35.5)} \text{ moles of AgCl} \equiv \frac{x}{74.5} \text{ moles of AgCl}$$

Therefore, mass of AgCl is :

$$\frac{x}{74.5} \text{ moles of AgCl} = \frac{x}{74.5} \times (108 + 35.5) \text{ gm} = \frac{143.5x}{74.5} \text{ gm}$$

Similarly, applying mole concept to second equation,



$$\frac{y}{(39 + 127)} \text{ moles of KI} \equiv \frac{y}{(39 + 127)} \text{ moles of AgI} \equiv \frac{y}{166} \text{ moles of AgI}$$

Therefore, mass of AgI is :

$$\frac{y}{166} \text{ moles of AgI} = \frac{y}{166} \times (108 + 127) \text{ gm} = 235 \frac{y}{166} \text{ gm}$$

According to question,

$$\frac{143.5x}{74.5} + \frac{235y}{166} = 3.8$$

In order to render coefficient of first term of the equation equal to 1 and hence simplify the equation, we multiply the equation by $\frac{74.5}{143.5}$,

$$x + \frac{74.5 \times 235y}{143.5 \times 166} = \frac{3.8 \times 74.5}{143.5}$$

$$\Rightarrow x + 0.73y = 1.97$$

Thus, we have two linear equations and two unknowns. Substituting for y in terms of x from first linear equation derived earlier, we have :

$$\Rightarrow x + 0.73(2.2 - x) = 1.97$$

$$\Rightarrow x + 1.61 - 0.73x = 1.97$$

$$\Rightarrow 0.27x = 0.36$$

$$\Rightarrow x = 1.34 \text{ gm}$$

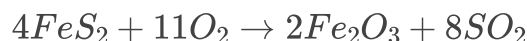
$$\Rightarrow y = 2.2 - x = 2.2 - 1.34 = 0.86 \text{ gm}$$

Chain reaction

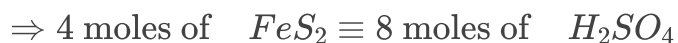
A chemical process involves multiple reactions in which product of one reaction becomes reactant in the second reaction. Consider example of formation of sulphuric acid from pyrite(FeS_2) :



Here, first reaction supplies SO_2 required as reactant in the second reaction. We, therefore, need to multiply second reaction 4 times so that SO_2 molecules are balanced. Similarly, third reaction should be multiplied by 8 to match $8SO_3$ molecules produced in the second reaction. Thus, balanced chain reaction is :



From balanced chain equations, we conclude that :



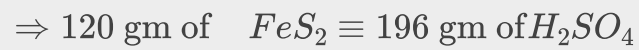
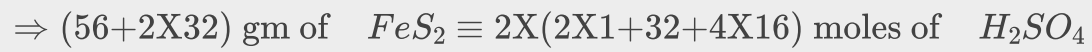
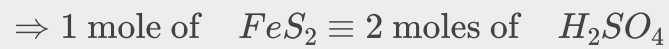
Alternatively, we can argue that one molecule of FeS_2 contains 2 atoms of Sulphur(S). On the other hand, one molecule of H_2SO_4 contains 2 atoms of Sulphur(S). Further, there is no loss or gain of Sulphur in chain reactions. Hence, to conserve mass of sulphur,



Example:

Problem : How many grams of sulphuric acid can be obtained from 100 gm of pyrite?

Solution : Here,



Applying unitary method,

$$\Rightarrow \text{mass of } H_2SO_4 = \frac{196}{120} \times 100 = 163.33 \text{ gm}$$

Molar concentration

The idea of mole concept is simple. It neatly relates various reactants and products in the ratio of whole numbers. There is, however, one hitch in applying this concept. The reactants or products may not necessarily be participating in its pure form. Consider the reaction :



Here, magnesium is used in its pure solid form. The hydrogen gas is evolved in pure gaseous form. On the other hand, Hydrochloric acid is used as a solution of a specific concentration in water.

Thus, magnesium and hydrogen exist in pure form. We can find moles of solid magnesium by using its molecular weight. Similarly, we can determine moles of pure hydrogen gas using Avogadro's hypothesis. In the case of hydrochloric acid, however, the acid in the form of solute participates in reaction – not the solvent i.e. water. Clearly, we need to find a way to connect the concentration of HCl to mass or moles. In this module, we shall exactly do the same by defining different concentration terms of the solution and its relation with mass or moles of the solute as involved in the reaction.

Solution

A solution is a homogeneous mixture of two or more components. The substance present in smaller proportions is called solute and the substance in larger proportion is called the solvent.

Solution comprises of solute and solvent. In expressing concentration of solution, we make use of the fact that mass is conserved,

$$\text{Mass of solution}(W_S) = \text{Mass of solute}(W_B) + \text{Mass of solvent}(W_A)$$

The concentration, however, need not be necessarily expressed in terms of mass (w). We may choose volume (v) also depending upon measuring convenience. Sometime, we may express concentration as combination of mass (w) and volume (v).

Concentration of a solution is basically measurement of solute (B) with respect to solution(S) or solvent(A). With the only exception of molality, concentration is expressed as a comparison of the quantity of solute (B) to that of solution (A+B). In the case of molality, it is comparison of solute (B) to that of solvent (A). Further, this comparative ratio is either a number or percentage (%).

There are large numbers of concentration measuring terms. They are basically classified under following three categories :

- Measurement based on mass/volume : mass percentage (w/w), volume percentage (v/v), strength of solution (w/v)
- Measurement based on molecular weight (moles) : molarity (M), molality (m)
- Measurement based on equivalent weight (gram - equivalents) : normality (N)

Measurements based on mass/volume

Mass percentage (w/w)

The mass percentage is expressed as :

$$\text{Mass percentage}(x) = \frac{\text{Mass of solute}(B)}{\text{Mass of solution}(A + B)} \times 100$$

$$\Rightarrow \text{Mass percentage}(x) = \frac{W_B}{W_S} \times 100 = \frac{W_B}{W_A + W_B} \times 100$$

If we measure mass in grams, we can rewrite the expression :

$$\Rightarrow \text{Mass percentage}(x) = \frac{g_B}{g_S} \times 100 = \frac{g_B}{g_A + g_B} \times 100$$

Sometimes, we may opt to express concentration simply as fraction. In this case, we are not required to multiply ratio by 100,

$$\text{Mass fraction} = \frac{W_B}{W_A + W_B} = \frac{g_B}{g_A + g_B}$$

Example:

Problem : One litre of oxalic acid of density 1.08 gm/cc contains 3.24 gm of oxalic acid. Find its mass percentage.

Solution : The mass of solute (oxalic acid) is given. We need to find the mass of the solution to determine mass percentage.

$$g_S = V_S \times \rho_S = 1000 \times 1.08 = 1080 \text{ gm}$$

$$\Rightarrow \text{Mass percentage}(x) = \frac{g_B}{g_A + g_B} \times 100 = \frac{3.28}{1008} \times 100 = 0.3$$

Example:

Problem : One kg solution has 0.6 % of urea (w/w) in it. If the molar mass of urea is 60 gm/mol^{-1} , then determine the moles of urea present in the solution.

Solution : The mass of solute (oxalic acid) is obtained as :

$$g_B = \frac{x \times g_S}{100} = \frac{0.6 \times 1000}{100} = 60 \text{ gm}$$

$$n_B = \frac{g_A}{M_O} = \frac{60}{60} = 1$$

Mass percentage of oleum

Sulphuric acid is formed by passing SO_3 gas through water in accordance with following chemical equation :



When all water molecules combine to form sulphuric acid, there remains free SO_3 molecules. Oleum is the name given to this mixture of concentrated sulphuric acid solution and free SO_3 . From the point of view reaction between oleum and other solution, SO_3 molecules are as good as sulphuric acid molecule as it reacts with available water molecules to form sulphuric acid molecule.

If an oleum solution has x percent of free SO_3 (x gm in 100 gm of oleum), then the equivalent amount of sulphuric acid is calculated using mole concept :

$$\Rightarrow 1 \text{ mole of } SO_3 \equiv 1 \text{ mole of } H_2SO_4$$

$$\Rightarrow 80 \text{ gm of } SO_3 \equiv 98 \text{ gm of } H_2SO_4$$

H_2SO_4 that can be formed from x gm of SO_3 is $\frac{98x}{80}$. Total mass of H_2SO_4 is sum of H_2SO_4 in the liquid form and H_2SO_4 that can be formed when H_2SO_4 reacts with water :

$$\Rightarrow \text{total mass of } H_2SO_4 = 100 - x + \frac{98x}{80} = 100 + \frac{18x}{80}$$

Considering equivalent H_2SO_4 mass in calculation, the mass percentage of H_2SO_4 in oleum is given as :

$$\Rightarrow y = \frac{\text{Total mass of } H_2SO_4}{\text{mass of oleum}} = \frac{100 + \frac{18x}{80}}{100} \times 100 = 100 + \frac{18x}{80}$$

Clearly, equivalent H_2SO_4 mass percentage is more than 100 %.

Volume percentage (v/v)

The volume percentage is expressed as :

$$\text{Volume percentage}(x) = \frac{\text{Volume of solute}(B)}{\text{Volume of solution}(A + B)} \times 100$$

$$\Rightarrow \text{Volume percentage}(x) = \frac{V_B}{V_S} \times 100 = \frac{V_B}{V_A + V_B} \times 100$$

Strength of solution (w/v)

The strength of solution is expressed as :

$$\text{Strength of solution}(S) = \frac{\text{Mass of solute (B) in grams}}{\text{Volume of solution in litres}}$$

$$\Rightarrow S = \frac{g_B}{V_L}$$

The unit of strength is “grams/liters”. Note that strength of solution is not a percentage – rather a number. The symbol V_L denotes volume of solution in litres, whereas V_{CC} denotes volume of solution.

in cc. If volume is expressed in cc, then the formula of strength is :

$$\Rightarrow S = \frac{g_B \times 1000}{V_{cc}}$$

Example:

Problem : Determine the numbers of moles of sulphuric acid present in 500 cc of 392 gm/litre acid solution.

Solution : In order to find the moles of sulphuric acid, we need to find its mass in the given volume.

$$g_B = S \times V_L = 392 \times 0.5 = 196 \text{ gm}$$

The moles of H_2SO_4 ($M_0 = 2 + 32 + 4 \times 16 = 98$) is :

$$n_B = \frac{196}{98} = 2$$

Molar concentration

The conversion of concentration of the solution into molar mass of the solute is a two steps process. In the first step, we calculate the mass of the solute and then in second step we divide the mass of the solute by molecular weight to determine the moles of solute present in the solution. We can think of yet a direct measurement of molar concentration. This will enable us to calculate moles of solute in one step.

Mole fraction

Mole fraction of solute (χ_B) is defined as :

$$\begin{aligned} \text{Molefraction}(\chi_B) &= \frac{\text{Mole of solute}(B)}{\text{Mole of solvent}(A) + \text{Mole of solute}(B)} \\ \Rightarrow \chi_B &= \frac{n_B}{n_A + n_B} \end{aligned}$$

Similarly, mole fraction of solvent (B) or other component of solution is :

$$\Rightarrow \chi_A = \frac{n_A}{n_A + n_B}$$

Clearly,

$$\Rightarrow \chi_A + \chi_B = 1$$

Example:

Problem : The mass fraction of ethyl alcohol in a sample of 1 kg of aqueous ethyl alcohol solution is 0.23. Determine mole fraction of ethyl alcohol and water in the solution.

Solution : The mass of ethyl alcohol and water are calculated as :

$$\Rightarrow g_B = \text{mass fraction} \times \text{mass of solution} = 0.23 \times 1000 = 230 \text{ gm}$$

$$\Rightarrow \text{mass of solvent} = g_A = \text{mass of solution} - \text{mass of ethyl alcohol} = 1000 - 230 = 770 \text{ gm}$$

The moles of ethyl alcohol and water are :

$$\Rightarrow n_B = \frac{230}{M_{C_2H_5OH}} = \frac{230}{2 \times 12 + 5 \times 1 + 16 + 1} = \frac{230}{46} = 5$$

$$\Rightarrow n_A = \frac{770}{M_{H_2O}} = \frac{770}{18} = \frac{770}{18} = 42.8$$

The mole fraction of ethyl alcohol and water are :

$$\Rightarrow \chi_B = \frac{n_B}{n_A + n_B} = \frac{5}{42.8 + 5} = \frac{5}{47.8} = 0.104$$

$$\Rightarrow \chi_A = 1 - 0.104 = 0.896$$

Example:

Problem : In a container, 14 gm nitrogen is mixed with 2 gm of hydrogen gas to form ammonia gas. The amount of ammonia formed is 5.1 gm. Determine mole fractions of ammonia in the container.

Solution : Here, moles of nitrogen and hydrogen present in the container are :

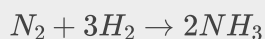
$$\text{Moles of nitrogen} = \frac{14}{2 \times 14} = 0.5$$

$$\text{Moles of hydrogen} = \frac{2}{1 \times 2} = 1$$

In order to determine mole fraction, we need to know the moles of gases remaining after the reaction. We can know the moles of gas provided we know the extent reaction takes place. The mass of product is known here. Using chemical equation, we can determine the moles of nitrogen and hydrogen used.

$$\text{Moles of ammonia produced} = \frac{5.1}{(14 + 3 \times 1)} = \frac{5.1}{17} = 0.3$$

The chemical equation is :



Applying mole concept :



Thus, moles of nitrogen and hydrogen gas consumed are :

$$\text{Moles of } N_2 \text{ consumed} = \frac{1}{2} \times 0.3 = 0.15$$

$$\text{Moles of } H_2 \text{ consumed} = \frac{3}{2} \times 0.3 = 0.45$$

Clearly, reaction does not exhaust either of gases. The moles remaining in the container after reaction are :

$$\text{Moles of } N_2 \text{ remaining} = 0.5 - 0.15 = 0.35$$

$$\text{Moles of } H_2 \text{ remaining} = 1.0 - 0.45 = 0.55$$

$$\text{Moles of } NH_3 \text{ produced} = 0.3$$

$$\text{Mole fraction of } NH_3 = \frac{0.3}{0.3 + 0.35 + 0.55} = \frac{0.3}{1.2} = 0.25$$

Molarity

Molarity of a solution with respect to solute is defined as :

$$\begin{aligned} \text{Molarity}(M) &= \frac{\text{Moles of solute}(B)}{\text{Volume of solution in litres}} \\ \Rightarrow M &= \frac{n_B}{V_L} \end{aligned}$$

Its unit is moles/ litres. In case we consider volume in ml i.e. cc, then the expression of molarity is given as :

$$\Rightarrow M = \frac{n_B}{V_{CC}} \times 1000 = \frac{\text{Milli-moles of B}}{V_{CC}}$$

If volume (litres) of a solution of known molarity is known, then number of moles of solute is obtained as :

$$\Rightarrow \text{Moles of B}(n_B) = \text{Molarity} \times \text{Volume in litres} = MV_L$$

Similarly,

$$\Rightarrow \text{Milli-moles of B} = \text{Molarity} \times \text{Volume in litres} = MV_{CC}$$

Example:

Problem : Determine (i) molarity of 750 cc NaOH solution containing 40 gm NaOH (ii) moles and milli-moles of NaOH in 500 ml of 0.4 M NaOH solution and (iii) mass of NaOH in 500 ml of 0.2 M NaOH solution.

Solution : (i) In the first part, volume is given in cc. Hence, we use the formula :

$$\Rightarrow M = \frac{n_B}{V_{CC}} \times 1000$$

In order to use this formula, we need to find the moles present. Here, molecular weight of NaOH is $23+16+1 = 40$. Hence,

$$n_B = 40/40 = 1$$

Putting values in the expression, we have :

$$\Rightarrow M = \frac{1}{750} \times 1000 = 1.33M$$

(ii) Moles of solute is :

$$\Rightarrow n_B = \frac{0.4 \times 500}{1000} = 0.2$$

$$\Rightarrow \text{Millimoles of solute} = MV_{CC} = 0.4 \times 500 = 200$$

(iii) Moles of solute is :

$$\Rightarrow n_B = \frac{0.2 \times 500}{1000} = 0.1$$

The mass of NaOH is :

$$\Rightarrow g_B = n_B \times M_{NaOH} = 0.1 \times 40 = 4 \text{ gm}$$

Example:

Problem : Two litres of a solution is prepared, which contains 44.4 gm of calcium hydro-oxide. Find milli-moles of calcium hydro-oxide in 100 ml sample of the solution.

Solution : Here we first need to determine the molarity of the solution as :

$$M = \frac{n_B}{V_L}$$

The moles of calcium hydro-oxide is :

$$\Rightarrow n_B = \frac{44.4}{M_{Ca(OH)_2}} = \frac{44.4}{40 + 2 \times (16 + 1)} = \frac{44.4}{74} = 0.6$$

Putting this in the formula, we have :

$$\Rightarrow M = \frac{n_B}{V_L} = \frac{0.6}{2} = 0.3M$$

The 100 ml sample has the same molarity as that of the bulk solution. Hence,

$$\Rightarrow \text{Milli-moles} = MV_{CC} = 0.3 \times 100 = 30$$

Example:

Problem : What is molarity of pure water assuming its density 1 gm/cc ?

Solution : Pure water is one component system. According to definition, molarity is given as :

$$M = \frac{n_B}{V_L}$$

Let $V_L = 1$ litre. The mass of 1 litre water is 1000 gm as density is 1 gm/cc. The number of moles in 1000 gm is :

$$n_B = \frac{1000}{18} = 55.56$$

Putting this value in the expression of molarity, we have :

$$\Rightarrow M = \frac{n_B}{V_L} = \frac{55.56}{1} = 55.56$$

Molarity and strength of solution

Molarity is defined as :

$$M = \frac{n_B}{V_L}$$

Substituting for expression of moles,

$$\Rightarrow M = \frac{n_B}{V_L} = \frac{g_B}{M_O V_L}$$

But we know that ratio of mass of solute in gram and volume of solution in litres is “strength of solution” :

$$S = \frac{g_B}{V_L}$$

Combining two equations, we have :

$$\Rightarrow M = \frac{g_B}{M_O V_L} = \frac{S}{M_O}$$

$$\Rightarrow S = M M_O$$

Molarity and mass percentage

Let mass percentage be x . It means that 100 gm of solution contains “ x ” gm of solute (B). Also let “ d ” be the density of solution in gm/cc. Then, 1000 cc of solution weighs $1000d$ gm. This further implies that :

$$\text{Solute "B" in } 1000d \text{ gm of solution (i.e. 1 litre solution)} = \frac{x}{100} \times 1000d = 10xd$$

Now molarity is :

$$M = \frac{n_B}{V_L} = \frac{g_B}{M_O V_L} = \frac{10xd}{M_O \times 1} = \frac{10xd}{M_O}$$

This relation means that we can determine molarity of a solution, if we know (i) molecular weight (ii) mass percentage and (iii) density of the solution.

Example:

Problem : Sulphuric acid solution of density 1.8 gm/cc contains 24.5% acid by weight. What is molarity of the solution?

Solution : Here,

$$\text{Mass percentage, } x = 24.5$$

$$\text{Density in gm/cc, } d = 1.8$$

$$\text{Molecular weight of } H_2SO_4 = 2 \times 1 + 32 + 4 \times 16 = 98$$

Molarity of the solution is :

$$\Rightarrow M = \frac{10xd}{M_O} = \frac{10 \times 24.5 \times 1.8}{98} = 4.5M$$

Molal concentration

Molality (m) is also a measurement of molar concentration like molarity (M). We have seen that molarity(M) is a convenient measurement of the concentration of solution as it allows us to directly compute moles of solute present in the solution. There is, however, a problem in reporting concentration of a solution in terms of molarity. Recall that it is equal to numbers of moles of solute divided by volume of solution in litres. The molar ratio has volume of the solution in the denominator. This means that molarity(M) of a given solution will change with temperature as volume of solution will change with temperature. This is a major handicap as reported concentration needs to be reliable and constant anywhere irrespective of temperature. In this backdrop, molality(m) is measurement of concentration aiming to remove this shortcoming associated with measurement in molarity (M).

Molality(m) also differs to other measurements in yet another important aspect. It involves the ratio of measurement of solute and solvent – not that of solute and solution. This difference is important to be kept in mind while computing quantities and converting measurement units from one to another.

The major objective of this module is to develop skills to convert measurement of concentration from one measurement type to another.

Molality of a solution with respect to solute is defined as :

$$\text{Molality}(m) = \frac{\text{Moles of solute (B)}}{\text{Mass of solvent (A) in Kg}}$$
$$\Rightarrow m = \frac{n_B}{w_{\text{Akg}}}$$

Its unit is moles/ kg. In case we consider mass of solvent in gm, then the expression of molality is given as :

$$\Rightarrow m = \frac{n_B}{g_A} \times 1000 = \frac{\text{Milli-moles of B}}{g_A}$$

If mass of solvent of a solution of known molality is known, then number of moles of solute is obtained as :

$$\Rightarrow \text{Moles of solute, B} = \text{Molality} \times \text{Mass of solvent in kg}$$

Similarly,

$$\Rightarrow \text{Milli-moles of B} = \text{Molality} \times \text{Mass of solvent (A) in gm}$$

Example:

Problem : 11.7 gm of sodium chloride is dissolved in 400 ml of water. Find molality of the solution.

Solution : Here,

$$\Rightarrow \text{Moles of sodium chloride} = \frac{11.7}{(23 + 35.5)} = \frac{11.7}{58.5} = 0.2$$

$$\Rightarrow \text{Mass of the solvent} = 400 \times 1 = 400 \text{ gm} = 0.4 \text{ kg}$$

$$\Rightarrow \text{Molality, } m = \frac{0.2}{0.4} = 0.5 \text{ m}$$

Molality in terms of molarity and density of solution

Molality and Molarity are linked to each other through density of solution. Beginning with the definition of molarity, a solution of molarity “M” means that 1 litre of solution contains “M” moles of solute. If the density of the solution is “d” in gm/cc, then

$$\text{Mass of 1 litre solution in gm} = 1000d$$

$$\text{Mass of the solute in gm in 1 litre solution} = \text{nos of moles} \times \text{molecular weight} = MM_O$$

$$\Rightarrow \text{Mass of the solvent in gm in 1 litre solution} = 1000d - MM_O$$

We need to calculate mass of solvent in kg to calculate molality(m) :

$$\Rightarrow \text{Mass of the solvent in kg in 1 litre solution} = (1000d - MM_O)/1000$$

Hence, molality,

$$m = \frac{n_B}{W_{\text{Akg}}} = \frac{M}{\frac{1000d - MM_O}{1000}} = \frac{1000M}{1000d - MM_O}$$

We should note that "density of solution (d)" and "strength of solution (S)" differ. Density of solution (d) is ratio of mass of solution (solute + solvent) in gm and volume of solution in cc. It has the unit of gm/cc. On the other hand, strength of solution (S) is ratio of mass of solute in gm and volume of solution in litre. It has the unit of gm/litre.

Example:

Problem : The density of 3M sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) solution is 1.25 gm/cc. Calculate molality of Na^+ and



ions.

Solution : We can use the formula to calculate molality of the sodium thiosulphate :

$$\Rightarrow m = \frac{1000M}{1000d - MM_O} = \frac{1000 \times 3}{1000 \times 1.25 - 3 \times (2 \times 23 + 2 \times 32 + 3 \times 16)}$$

$$\Rightarrow m = \frac{3000}{1250 - 474} = \frac{3000}{776} = 3.866$$

Alternatively, we can proceed with the basic consideration in place of using formula. Since molarity of solution is 3M, it means that 1 litre of solution contains 3 moles of sodium thiosulphate. We can use density to find the mass of the 1 litre solvent.

$$\Rightarrow \text{Mass of solution} = 1000 \times 1.25 = 1250 \text{ gm}$$

$$\Rightarrow \text{Mass of 3 moles of sodium thiosulphate} = 3M_{Na_2S_2O_3} = 3 \times (2 \times 23 + 2 \times 32 + 3 \times 16)$$

$$\Rightarrow \text{Mass of 3 moles of sodium thiosulphate} = 3 \times (46 + 64 + 48) = 3 \times 158 = 474 \text{ gm}$$

$$\Rightarrow \text{Mass of solvent} = 1250 - 474 = 776 \text{ gm} = 0.776 \text{ kg}$$

$$\Rightarrow \text{Molality of sodium thiosulphate} = \frac{3}{0.776} = 3.866 \text{ m}$$

We are, however, required to calculate molality of ions. We see that one mole is equivalent to 2 moles of sodium ion and 1 mole of thiosulphate ion :



Hence,

$$\Rightarrow \text{Molality of } Na^+ = 2 \times 3.866 = 7.732 \text{ m}$$

$$\Rightarrow \text{Molality of } S_2O_3^{--} = 3.866 \text{ m}$$

Density of solution in terms of molarity and molality

Working on the relation of molality developed in previous section :

$$m = \frac{1000M}{1000d - MM_O}$$

$$\Rightarrow \frac{1}{m} = \frac{1000d - MM_O}{1000M} = \frac{d}{M} - \frac{M_O}{1000}$$

$$\Rightarrow d = M \left(\frac{1}{m} + \frac{M_O}{1000} \right)$$

Example:

Problem : The molality and molarity of a solution of sulphuric acid are 90 and 10 respectively Determine density of the solution.

Solution : Using relation :

$$\Rightarrow d = M \left(\frac{1}{m} + \frac{M_O}{1000} \right)$$

$$\Rightarrow d = 10 \left(\frac{1}{90} + \frac{98}{1000} \right) = 10 \times (0.011 + 0.098) = 10 \times 0.0991 = 9.91 \text{ gm/cc}$$

Molality in terms of density of solution and strength of solution

We need to know the moles of solute and mass of solvent in kg to determine molality. Now, strength of solution (S) is equal to mass of the solute in gm in 1 litre of solution. Hence,

Mass of the solute in gm in 1 litre of solution = S

$$\text{Moles of the solute} = \frac{S}{M_O}$$

Mass of 1 litre solution in gm = $1000d$

Mass of the solvent in gm in 1 litre of solution = $1000d - S$

Mass of the solvent in kg in 1 litre of solution = $\frac{(1000d - S)}{1000}$

The molality is :

$$\Rightarrow m = \frac{n_B}{W_{\text{Akg}}} = \frac{\frac{S}{M_O}}{\frac{(1000d - S)}{1000}} = \frac{1000S}{M_O(1000d - S)}$$

Example:

Problem : A solution has 392 gm of sulphuric acid per litre of solution. If the density of the solution is 1.25 gm/cc, find molality of the solution.

Solution : Using relation :

$$\Rightarrow m = \frac{1000S}{M_O(1000d - S)} = \frac{1000 \times 392}{98 \times (1000 \times 1.25 - 392)} = 4.73 \quad m$$

Molality in terms of mole fraction and molecular weight

Molality is defined as :

$$m = \frac{n_B}{W_{Akg}} = \frac{n_B}{g_A} \times 1000 = \frac{n_B}{n_A M_A} \times 1000$$

$$\Rightarrow n_B = \frac{m n_A M_A}{1000}$$

On the other hand, mole fraction with respect to solute B is given by :

$$\chi_B = \frac{n_B}{n_A + n_B}$$

Substituting for n_A , we have :

$$\Rightarrow \chi_B = \frac{\frac{m n_A M_A}{1000}}{n_A + \frac{m n_A M_A}{1000}} = \frac{m M_A}{1000 + m M_A}$$

$$\Rightarrow 1000 \chi_B + m M_A \chi_B = m M_A$$

$$\Rightarrow m M_A (1 - \chi_B) = 1000 \chi_B$$

$$\Rightarrow m = \frac{1000 \chi_B}{(1 - \chi_B) M_A}$$

Similarly, we can express molality in terms of mole fraction with respect to solvent (A) as :

$$\Rightarrow m = \frac{1000(1 - \chi_A)}{\chi_A M_A}$$

Gram equivalent concept

Mole concept is based on molecular weight. An equivalent concept is “gram equivalent weight” or “gram equivalent” concept. It is based on equivalent weight. Equivalent weight is measure of mass proportion of an element, compound or ion in which it combines with the mass of other chemical entities. Mass of one gram equivalent, like its mole counterpart, is equal to mass in gram, which is numerically equal to equivalent weight.

Equivalent weight (E)

Equivalent weight unlike molecular weight is proportional mass of chemical entities which combine or displace other chemical entities.

Equivalent weight

It is defined as the mass of an element/compound/ion which combines or displaces 1 part of hydrogen or 8 parts of oxygen or 35.5 parts of chlorine by mass.

It is not always possible to apply this classic definition to determine equivalent weights of chemical entities. It is so because, we can not conceive of reactions involving chemical entities with three named reference of hydrogen, oxygen and chlorine. Generally, we are limited to determination of equivalent weights of elements and few compounds by using this definition of equivalent weight. A more workable definition is given as :

$$\text{Equivalent weight, } E = \frac{\text{Molecular weight}}{\text{Valence factor}} = \frac{M_O}{x}$$

Clearly, determination of equivalent weight amounts to determining valence factor “x”. Here, we shall classify chemical entities and the techniques to determine “x”.

Equivalent weight of an element

In the case of an element, the equivalent weight is defined as :

$$\text{Equivalent weight, } E = \frac{\text{Atomic weight}}{\text{Valency}} = \frac{A}{x}$$

Note that atomic weight substitutes molecular weight and valency substitutes valence factor in the definition. Valencies of hydrogen, calcium and oxygen are 1, 2 and 2 respectively. Hence, their equivalent weights are $1/1 = 1$, $40/2 = 20$ and $16/2 = 8$ respectively.

Equivalent weight of an acid

The valence factor of an acid is equal to its basicity. The basicity of an acid is equal to furnishable hydrogen ion (proton) in its aqueous solution. Importantly, basicity is not same as the number of hydrogen atoms in acid molecule. Consider acetic acid (CH_3COOH). It contains 4 hydrogen atoms in it, but only 1 furnishable hydrogen ion. As such, basicity of acetic acid is 1. With this background, we define equivalent weight of an acid as :

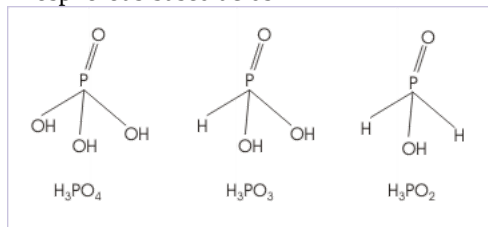
$$\text{Equivalent weight, } E = \frac{\text{Molecular weight of acid}}{\text{Basicity}}$$

Basicity of sulphuric acid is 2. Hence, equivalent weight of sulphuric acid (H_2SO_4) is $(2 \times 1 + 32 + 4 \times 16)/2 = 98/2 = 49$. Similarly, basicity of oxalic acid is 2. Hence, equivalent weight of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is $(2 \times 1 + 2 \times 12 + 4 \times 16)/2 = 90/2 = 45$.

Phosphorous based acids like phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3) and hypo-phosphorous acid (H_3PO_2) need special mention here to understand their basicity. The structures of three acids are shown here.

From the structure, it appears that these compounds may furnish OH ions, but bond strengths between phosphorous and oxygen (P-O) and phosphorous and hydrogen (P-H) are stronger than between oxygen and hydrogen (O-H) in –OH group. As such, these molecules release hydrogen ions from –OH group and behave as acid. Clearly, basicities of phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3) and hypo-phosphorous acid (H_3PO_2) are 3, 2 and 1 respectively.

Phosphorous based acids



Furnishable hydrogen ions of acids

Equivalent weight of a base

The valence factor of a base is equal to its acidity. The acidity of a base is equal to furnishable hydroxyl ion (OH-) in its aqueous solution. With this background, we define equivalent weight of a base as :

$$\text{Equivalent weight, } E = \frac{\text{Molecular weight of base}}{\text{Acidity}}$$

Acidity of KOH is 1, whereas acidity of $Ca(OH)_2$ is 2. Hence, equivalent weight of KOH is $(39 + 16 + 1)/1 = 56/1 = 56$. Similarly, equivalent weight of $Ca(OH)_2$ is $\{40 + 2 \times (16+1)\}/2 = 74/2=37$.

Equivalent weight of a compound

The valence factor of a compound depends on the manner a compound is involved in a reaction. The compounds of alkali metal salts and alkaline earth metal salts are, however, constant. These compounds are ionic and they dissociate in ionic components in aqueous solution. In this case, valence factor is equal to numbers of electronic charge on either cation or anion.

$$\text{Equivalent weight, } E = \frac{\text{Molecular weight of compound}}{\text{Numbers of electronic charge on cation or anion}}$$

The numbers of electronic charge on cation of $NaHCO_3$ is 1. Hence, equivalent weight of $NaHCO_3$ is $(23 + 1 + 12 + 3 \times 16)/1 = 84$.

If we look at the defining ratio of equivalent weight of a compound (AB) formed of two radicals (say A and B), then we can rearrange the ratio as :

$$\text{Equivalent weight, } E = \frac{\text{Molecular weight of Radical A}}{\text{Numbers of electronic charge}} + \frac{\text{Molecular weight of Radical B}}{\text{Numbers of electronic charge}}$$

Thus,

$$\Rightarrow \text{Equivalent weight of AB} = \text{Equivalent weight of A} + \text{Equivalent weight of B}$$

Equivalent weight of an ion

The valence factor of an ion is equal to numbers of electronic charge on the ion. Therefore, we define equivalent weight of an ion as :

$$\text{Equivalent weight, } E = \frac{\text{Molecular weight of ion}}{\text{Numbers of electronic charge}}$$

The numbers of electronic charge on carbonate ion (CO_3^{2-}) is 2. Hence, equivalent weight of carbonate ion is $(12 + 3 \times 16)/2 = 60/2 = 30$. Similarly, equivalent weight of aluminum ion (Al^{3+}) is $27/3 = 9$.

Equivalent weight of an oxidizing or reducing agent

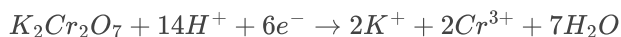
In a redox reaction, one of the reacting entities is oxidizing agent (OA). The other entity is reducing agent (RA). The oxidizer is recipient of electrons, whereas reducer is releaser of electrons. The valence factor for either an oxidizing or reducing agent is equal to the numbers of electrons transferred from one entity to another.

$$\text{Equivalent weight, } E = \frac{\text{Molecular weight of compound}}{\text{Numbers of electrons transferred in redox reaction}}$$

Alternatively,

$$\text{Equivalent weight, } E = \frac{\text{Molecular weight of compound}}{\text{Change in oxidation number in redox reaction}}$$

Potassium dichromate in acidic medium is a strong oxidizer. It means it gains electrons during redox reaction. Potassium dichromate in acidic solution results in :



$$\text{Equivalent weight of } K_2Cr_2O_7 = \frac{294.2}{6} = 49$$

Study of redox reaction is in itself an exclusive and extensive topic. We shall, therefore, discuss redox reaction separately.

Gram equivalent(geq)

It is equal to mass in grams numerically equal to equivalent weight. If the mass of a chemical entity is “g” grams, then the given mass contains gram equivalents given by :

$$\text{Gram equivalent (geq)} = \frac{g}{E}$$

This formula is widely used to express grams of substance in terms of gram equivalent and vice-versa.

Relation between moles and gram equivalents (geq)

Gram equivalents is given by :

$$\text{geq} = \frac{g}{E}$$

Substituting for equivalent weight, we have :

$$g_{eq} = \frac{g}{E} = \frac{xg}{M_O}$$

Moles is given by :

$$n = \frac{g}{M_O}$$

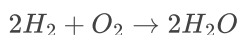
Combining expressions, we have :

$$g_{eq} = xn$$

$$\text{gram equivalent} = \text{valence factor} \times \text{moles}$$

Gram equivalent concept

Consider the example of formation of water :



Here, 2 moles of hydrogen combines with 1 mole of oxygen to form 2 moles of water molecule. In terms of mass, 4 gm of hydrogen combines with 32 gm of oxygen to form 36 gm of water molecule. The relevant proportions involved with this equation are :

$$\text{Coefficients of balanced equation} = 2:1:2$$

$$\text{Molecules/moles} = 2:1:2$$

$$\text{Mass} = 4:32:36 = 1:8:9$$

On the other hand, equivalent weights of hydrogen, oxygen and water are 1, 8 and 9. Clearly, proportion of mass in which chemical entities participate is exactly the proportion of equivalent weights! Note that mole concept depends on the coefficient of balanced chemical equation. On the other hand, the equivalent weight concept is independent of coefficient of balanced chemical equation. If we know that hydrogen and oxygen combines to form water molecule, then we can say straightway that entities are in the proportion of equivalent weights - without any reference to coefficients in the balanced chemical equation.

$$\text{equivalent weight of hydrogen} \equiv \text{equivalent weight of oxygen} \equiv \text{equivalent weight of water}$$

Note that there is no mention of coefficients of balanced chemical equation in the equivalent weight relation. We should, however, understand that two techniques of analyzing chemical reactions are essentially equivalent. We need to consider coefficients involved in balanced chemical equation for applying mole concept. On the other hand, coefficients are not considered when using equivalent weight concept, but we need to know the corresponding valence factor of each entity. It is important to realize that above relation is not a relation connected by "equal to (=)" sign. Rather, they are connected by equivalent sign (\equiv). As such, we still need to apply unitary method to analyze the relation.

Gram equivalent concept is a step head in this context. The gram equivalents of participating entities are same. For the case of formation of water, the proportion of mass of hydrogen, oxygen and water is 1 gm: 8 gm : 9 gm. Now, we know that the gram equivalents of entities are obtained by dividing mass by equivalent weight. Hence, gram equivalents of three entities are $1/1 = 1$, $8/8=1$ and $9/9 = 1$. Thus, gram equivalents of participating entities are same. If gram equivalents of hydrogen is 2, then gram equivalents of oxygen and water will also be 2. As such :

$$x \text{ gm equivalents of hydrogen} = x \text{ gm equivalents of oxygen} = x \text{ gm equivalents of water}$$

Significant aspect of this relation is that it is connected with equal to (=) sign and as such relieves us from applying unitary method altogether.

Example:

Problem : 100 gm of a mixture nitrates of two metals A and B are heated to constant weight of 50 gm, containing corresponding oxides of the metals. The equivalent weights of A and B are 103 and 31 respectively. What is the percentage composition of A and B in the mixture.

Solution : Here, we make use of the fact that :

Equivalent weight of metal nitrate =

Equivalent weight of metal nitrate = Equivalent weight of metal + Equivalent weight of nitrate - radical

Therefore,

$$\text{Equivalent weight of nitrate of A} = 103 + \frac{(14 + 3 \times 16)}{1} = 103 + 62 = 165$$

$$\text{Equivalent weight of oxide of A} = 103 + \frac{16}{2} = 103 + 8 = 111$$

$$\text{Equivalent weight of nitrate of B} = 31 + 62 = 93$$

$$\text{Equivalent weight of oxide of B} = 31 + 8 = 39$$

Let the mass of A in the mixture be x gm. Then mass of B is 100-x gm. Applying concept of equivalent weight concept to chemical reaction,

165 gm of nitrate of A yields 111 gm of A's oxide. Therefore, x gm of A's nitrate yields :

$$\Rightarrow \text{mass of A's oxide} = \frac{111x}{165} = 0.67x$$

Similarly,

$$\Rightarrow \text{mass of B's oxide} = \frac{39(100 - x)}{93} = 0.42 \times 100 - 0.42x = 42 - 0.42x$$

According to question,

$$\Rightarrow 0.67x + 42 - 0.42x = 50$$

$$\Rightarrow 0.25x = 50 - 42 = 8$$

$$\Rightarrow x = 32 \text{ gm}$$

$$\Rightarrow \text{Mass of A} = x = 32 \text{ gm}$$

$$\Rightarrow \text{Mass of B} = 100 - x = 68 \text{ gm}$$

Thus, mixture contains 32 % of A and 68 % of B.

Normality(N)

Normality is a measure of concentration of solution. It compares solute in terms of gram equivalents to the volume of solution in litres.

$$\text{Normality(N)} = \frac{\text{geq}}{V_L}$$

Its unit is geq/ litres. In case we consider volume in ml i.e. cc, then the expression of normality is given as :

$$\Rightarrow \text{Normality}(N) = \frac{\text{geq}}{V_{CC}} \times 1000 = \frac{\text{milli-gram equivalent}}{V_{CC}} = \frac{\text{meq}}{V_{CC}}$$

If volume of a solution of known normality is known, then number of gram equivalents or milli-gram equivalents of solute are obtained as :

$$\Rightarrow \text{geq} = NV_L$$

$$\Rightarrow \text{meq} = NV_{CC}$$

It is evident from the definition of normality that normality of a given bulk solution and that of a sample taken from it are same. For example, if we take 10 cc of sulphuric acid from 1 litre of 0.2N sulphuric acid solution, then normality of sample taken is also 0.2N. However, geq or meq will be different as the amount of solutes are different.

$$\text{meq in bulk solution} = 0.2 \times 1000 = 200$$

$$\text{meq in sample} = 0.2 \times 10 = 2$$

Example:

Problem : Find volume of 0.2 N solution containing 2.5 meq of solute.

Solution : The gram equivalent is given by :

$$\text{meq} = NV_{CC}$$

$$V_{CC} = \frac{\text{meq}}{N} = \frac{2.5}{0.2} = 12.5 \quad \text{cc}$$

Example:

Problem : How many grams of wet NaOH containing 10% water are required to prepare 1 litre of 0.1 N solution.

Solution : We can determine amount of NaOH for preparation of 1 litre of 0.1 N solution by using normality relation :

$$\text{geq} = NV = 0.1 \times 1 = 0.1$$

$$\Rightarrow \text{geq} = \frac{g}{E} = \frac{xg}{M_O}$$

The molecular weight of NaOH is 23+16+1= 40. Its valence factor is 1. Hence,

$$\Rightarrow g = \frac{\text{geq} \times M_O}{x} = \frac{0.1 \times 40}{1} = 4 \quad \text{gm}$$

But 100 gms of wet NaOH contain 88 gm NaOH. Applying unitary method, 4 gm of NaOH is present in wet NaOH given by :

$$\Rightarrow \text{Mass of wet NaOH} = \frac{4 \times 100}{88} = 4.55 \quad \text{gm}$$

Example:

Problem : Borax ($\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$) is a strong base in aqueous solution. Hydroxyl ions are produced by ionic dissociation as :



A solution of borax is prepared in water. The solution is completely neutralized with 50 ml of 0.1N HCl. Find the mass of borax in the solution. Consider atomic weight of boron 24 amu.

Solution : Applying gram equivalent concept,

$$\Rightarrow \text{meq of borax} = \text{meq of 50 ml 0.1N HCl}$$

$$\Rightarrow \text{meq of borax} = NV = 0.1 \times 50 = 5$$

Now, gram equivalent is connected to mass as :

$$\Rightarrow \text{meq} = \frac{1000g}{E} = \frac{1000xg}{M_O}$$

$$\Rightarrow g = \frac{\text{meq} \times E}{1000x} = \frac{1000xg}{M_O}$$

Molecular weight of borax is $2 \times 23 + 4 \times 24 + 7 \times 16 + 7 \times 18 = 380$. The valence factor of borax is 2 as one molecule of borax gives 2 hydroxyl ions. Putting values, we have,

$$\Rightarrow g = \frac{5 \times 380}{1000 \times 2} = 0.95 \text{ gm}$$

Relation between normality and molarity

Normality is defined as :

$$\text{Normality(N)} = \frac{\text{geq}}{V_L}$$

Substituting for gram equivalent,

$$\Rightarrow \text{Normality(N)} = \frac{\text{geq}}{V_L} = \frac{xM_O}{V_L}$$

where “x” is valance factor. Now, molarity is defined as :

$$M = \frac{M_O}{V_L}$$

Note that we have used the convention that “M” represents molarity and “ M_O ” or subscripted symbol “ M_{NH_3} ” represents molecular weight. Now, combining two equations, we have :

$$\Rightarrow N = xM$$

$$\text{Normality} = \text{valance factor} \times \text{Molarity}$$

Combining solutions of different normality

Let us consider two solutions : 100 ml of 1 N H_2SO_4 and 50 ml of 0.5 N H_2SO_4 . What would be the normality if these two volumes of different normality are combined?

In order to determine normality of the final solution, we need to find total milli-gram equivalents and total volume. Then, we can determine normality of the final solution by dividing total gram equivalents by total volume. Here,

$$\text{meq}_1 = N_1 V_1 = 1 \times 100 = 100$$

$$\text{meq}_2 = N_2 V_2 = 0.5 \times 50 = 25$$

Total meq is :

$$\Rightarrow \text{meq} = \text{meq}_1 + \text{meq}_2 = 100 + 25 = 125$$

Now, important question is whether we can combine volumes as we have combined milli-gram equivalents. Milli equivalents can be combined as it measures quantity i.e. mass of solutes, which is conserved. Can we add volumes like mass? Density of 1N solution has to be different than that of 0.5N solution. We need to account for the density of the individual solution. It means that given volumes can not be added. However, concentrations of these solutions are low and so the difference in densities of solutions. As a simplifying measure for calculation, we can neglect the minor change in volume of the resulting solution. With this assumption,

$$\Rightarrow \text{Total volume} = V_1 + V_2 = 100 + 50 = 150 \text{ ml}$$

The normality of the resulting solution is :

$$\Rightarrow N = \frac{125}{150} = \frac{5}{6} = 0.83$$

Normality of combination of different acids

Normality is based on the concept of gram-equivalent, which, in turn, depends on equivalent weights. The equivalent weight, on the other hand, is obtained by dividing molecular weight by basicity. The basicity, in turn, is equal to numbers of furnishable hydrogen ions. We may conclude that gram equivalent is amount of acid per furnishable hydrogen ion. Thus, we can see combination of acids (like sulphuric and hydrochloric acids) in terms of their ability of furnishing hydrogen ions. What it means that we can add gram equivalents of two acids to find total gram equivalents and find normality of resulting solution.

We can extend the concept to basic solution as well.

Example:

Problem : 500 ml of 0.5 N HCl is mixed with 20 ml of H_2SO_4 having density of 1.18 gm/cc and mass percentage of 10. Find the normality of resulting solution assuming volumes are additive.

Solution : Here, we first need to find normality of H_2SO_4 solution, whose density and mass percentage are given. Now, molarity of the solution is given as :

$$\Rightarrow M = \frac{10yd}{M_O} = 10 \times 10 \times \frac{1.18}{98} = 118/98 = 1.2M$$

Normality of sulphuric acid solution is :

$$\Rightarrow N = xM = 2 \times 1.2 = 2.4N$$

We can now determine total gram equivalents and total volumes to determine the normality of resulting solution.

$$\Rightarrow \text{meq}_1 = N_1 V_1 = 0.5 \times 500 = 250$$

$$\Rightarrow \text{meq}_2 = N_2 V_2 = 2.4 \times 20 = 48$$

Total meq is :

$$\Rightarrow \text{meq} = \text{meq}_1 + \text{meq}_2 = 250 + 48 = 298$$

$$\Rightarrow \text{Total volume} = V_1 + V_2 = 500 + 20 = 520 \text{ ml}$$

The normality of the resulting solution is :

$$\Rightarrow N = \frac{298}{520} = 0.57$$

Dilution

Dilution means adding solvent (A) to a solution (S). The amount of solute (B) remains constant, but the amount of solution increases. Dilution of solution is needed as solutions are purchased and stored in concentrated form; whereas we use solution of different concentration in accordance with the requirement of the application.

Concentration of solution is expressed in different concentration format as mass percent, mole fraction, molarity, normality or any other format. The underlying principle, here, is that quantity of solute remains the same before and after dilution.

Dilution of a solution of a given chemical entity can also be realized by mixing solution of higher concentration with solution of lower concentration. This mixing is equivalent to increasing amount of solvent. This aspect has already been dealt in the module titled “Gram equivalent concept”.

Mass percentage and dilution

Mass percentage is equal to percentage of mass of solute with respect to solution and is given by :

$$y = \frac{\text{Mass of solute(B)}}{\text{Mass of solution(S)}} = \frac{W_B}{W_S} \times 100 = \frac{g_B}{g_S} \times 100$$

Let 1 and 2 subscripts denote before and after states, then mass of solute before and after dilution is same :

$$W_{B_1} = W_{B_2}$$

$$y_1 W_{S_1} = y_2 W_{S_2}$$

Similarly,

$$y_1 g_{S_1} = y_2 g_{S_2}$$

Example:

Problem : How much water would you need to prepare 600 grams of a 4% (w/w) Hydrogen Peroxide (H_2O_2) solution using a solution of 20% (w/w) ?

Solution : Here,

$$g_{S_1} = 600 \text{ gm}$$

$$y_1 = 4$$

$$y_2 = 20$$

$$y_1 g_{S_1} = y_2 g_{S_2}$$

$$\Rightarrow 4 \times 600 = 20 \times g_{S_2}$$

$$\Rightarrow g_{S_2} = \frac{4 \times 600}{20} = 120 \text{ gm}$$

Total mass of 4% = mass of 20% solution + mass of water added

$$\text{mass of water added} = 600 - 120 = 480 \text{ gm}$$

Molarity and dilution

Molarity is equal to ratio of moles of solute and volume of solution and is given by :

$$M = \frac{\text{moles of solute}}{V_L} == \frac{\text{mill-moles of solute}}{V_{CC}}$$

Let 1 and 2 subscripts denote before and after dilution, then :

moles before dilution = moles after dilution

$$M_1 V_{L_1} = M_2 V_{L_2}$$

Similarly,

$$M_1V_{CC_1} = M_2V_{CC_2}$$

Example:

Problem : What volume of water should be added to 100 ml nitric acid having specific gravity 1.4 and 70% strength to give 1 M solution?

Solution : We first need to convert the given strength of concentration to molarity. Molarity is given by :

$$M = \frac{10yd}{M_O}$$

The specific gravity is 1.4 (density compared to water). Hence, density of solution is 1.4 gm/ml.

$$\Rightarrow M = \frac{10 \times 70 \times 1.4}{(1 + 14 + 3 \times 16)} = 15.55M$$

Applying dilution equation,

$$M_1V_{CC_1} = M_2V_{CC_2}$$

$$\Rightarrow 15.55 \times 100 = 1 \times V_2$$

$$\Rightarrow V_2 = 1555 \text{ ml}$$

$$\text{The volume of water to be added} = 1555 - 100 = 1455 \text{ ml}$$

Example:

Problem : In an experiment, 300 ml of 6.0 M nitric acid is required. Only 50 ml of pure nitric acid is available. Pure anhydrous nitric acid (100%) is a colorless liquid with a density of 1522 kg/m^3 . Would it be possible to carry out the experiment?

Solution : Here,

$$M_1 = 6M; \quad M_2 = ?; \quad V_{CC_1} = 300 \text{ ml}; \quad V_{CC_2} = ?$$

In order to apply dilution equation, we need to know the molarity of concentrated nitric acid. Now 1 litre pure concentrate weighs $1000 \times 1.522 = 1522$ gm. The number of moles in 1 litre of nitric acid is :

$$\Rightarrow n_B = \frac{1522}{(1 + 14 + 3 \times 16)} = 24.16$$

Hence, molarity of the nitric acid concentrate is 24.16 M.

Applying dilution equation,

$$\begin{aligned} M_1 V_{CC_1} &= M_2 V_{CC_2} \\ \Rightarrow V_{CC_2} &= \frac{M_1 V_{CC_1}}{M_2} = \frac{6 \times 300}{24.16} = 74.5 \text{ ml} \end{aligned}$$

It means requirement of concentrate (74.5 ml) is more than what is available (50 ml). As such, experiment can not be completed.

Example:

Problem : A 100 ml, 0.5 M calcium nitrate solution is mixed with 200 ml of 1.25M calcium nitrate solution. Calculate the concentration of the final solution. Assume volumes to be additive.

Solution : We first calculate milli-moles for each solution. Then, add them up to get the total moles present in the solution. Finally, we divide that total moles by the total volume.

$$\text{Milli-moles in the first solution} = M_1 V_{CC_1} = 100 \times 0.5 = 50$$

$$\text{Milli-moles in the second solution} = M_2 V_{CC_2} = 200 \times 1.25 = 250$$

$$\text{Milli-moles in the final solution} = 50 + 250 = 300$$

$$\text{Total volume of the solution} = 100 + 200 = 300 \text{ ml}$$

Hence, molarity of the final solution is :

$$M = \frac{\text{Milli-moles of solute}}{V_{CC}} = \frac{300}{300} = 1M$$

Alternative method

Molarity of the first solution when diluted to final volume of 300 ml is obtained as :

$$\begin{aligned}M_1V_{CC_1} &= M_2V_{CC_2} \\ \Rightarrow 0.5 \times 100 &= M_2 \times 300 \\ \Rightarrow M_2 &= \frac{50}{300} = \frac{1}{6}\end{aligned}$$

Molarity of the second solution when diluted to final volume of 300 ml is obtained as :

$$\begin{aligned}M_1V_{CC_1} &= M_2V_{CC_2} \\ \Rightarrow 1.25 \times 200 &= M_2 \times 300 \\ \Rightarrow M_2 &= \frac{250}{300} = \frac{5}{6}\end{aligned}$$

Hence, molarity of the final combined solution is :

$$M = \frac{1}{6} + \frac{5}{6} = 1$$

Normality and dilution

As there is no change in the amount of solute due to dilution, the amount expressed as gram equivalents should also remain same before and after dilution. Like in the case of molarity, we state the condition of dilution in terms of normality as :

$$\text{Gram equivalents in the solution} = N_1V_1 = N_2V_2$$

Example:

Problem : What volume of water should be added to 100 ml sulphuric acid having specific gravity 1.1 and 80% strength to give 1 N solution?

Solution : We first need to convert the given strength of concentration to Normality. For that we first calculate molarity and then use the formula : :

$$N = xM$$

Now, molarity is given by

$$M = \frac{10yd}{M_O}$$

The specific gravity is 1.4 (density compared to water). Hence, density of solution is 1.4 gm/ml.

$$\Rightarrow M = \frac{10 \times 80 \times 1.1}{(2 \times 1 + 32 + 4 \times 16)} = 8.98M$$

The valence factor of H_2SO_4 is 2. Hence,

$$\Rightarrow N = xM = 2 \times 8.98 = 17.96N$$

Applying dilution equation,

$$\begin{aligned} N_1V_{CC_1} &= N_2V_{CC_2} \\ \Rightarrow 17.96 \times 100 &= 1 \times V_2 \\ \Rightarrow V_2 &= 1796 \text{ ml} \end{aligned}$$

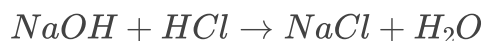
$$\text{The volume of water to be added} = 1796 - 100 = 1696 \text{ ml}$$

Neutralization reaction

Neutralization reaction refers to acid and base reaction producing salt and water. The equivalent amounts of acid react with base to form equivalent amounts of salt and water. When the reaction is complete, acid and base are said to neutralize each other. Since water is produced, neutralization reaction is also referred as “water forming reaction”.



Consider reaction like :



We can rewrite the reaction in ionic form as :



Essentially, neutralization reaction is double displacement reaction. Some definitions used in the study of neutralization reaction are :

Equivalence point : The state of acid base reaction when acid and base react in exact equivalent amounts as determined theoretically.

End point : The state of acid base reaction when acid and base react in exact equivalent amounts as determined practically (during titration). Clearly, end point volume measurement is slightly greater than that corresponding to equivalence point.

Neutral point : The state of acid-base reaction when product solution is neutral (pH=7).

The ionic salt formed from the reaction of strong acid [$H_2SO_4, HCl, HNO_3, H_3PO_4$] and strong base [$NaOH, KOH, Mg(OH)_2, Ca(OH)_2$] are pH neutral. Also, water is pH neutral. As such, strong acid and strong base reaction yields neutral products or product solution. In this case, equivalence and neutral points are same.

However, salts formed with other combinations like “strong acid - weak base” and “weak acid - strong base” are not neutral. They produce salts, which are either acidic or basic in nature. As such, pH of the product solution is not 7. Here, equivalence point is not same as neutral point.



We refer acid-base reaction as neutralization reaction even though products are not neutral (pH=7). As a matter of fact, product solution is acidic (pH<3) for strong acid –weak base

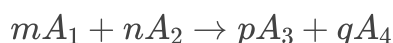
reaction. We need to add more of base solution beyond equivalence volume to make the product solution neutral. Similarly, product solution is basic ($\text{pH} > 7$) for weak acid-strong base reaction. Here, we need to add more acid beyond equivalence volume to make the product solution neutral.

Titration

The acid-base reaction involves completion of reaction in equivalent proportion of solutes in the solutions. The experimental process to study proportion of reacting volumes and calculation of mass/ concentration of solution is known as "titration". Completion of reaction is known by chemical indicator or by other means depending on the type of reaction involved. We shall study details of titration process separately.

Analyzing neutralization reaction

We treat neutralization reaction on similar footing as other reactions. Generally, it involves reaction between two solutions of certain concentrations. Clearly, it is helpful to describe analysis in terms of molarity or normality. For a generic consideration :



In terms of moles, we have :

$$m \text{ moles of } A_1 \equiv n \text{ moles of } A_2 \equiv p \text{ moles of } A_3 \equiv q \text{ moles of } A_4$$

$$mM_1V_1 \equiv nM_2V_2 \equiv pM_3V_3 \equiv qM_4V_4$$

Consideration in molarity gives a relation that needs to be analyzed using unitary method. It is important to realize that this is not a relation which are not connected with "equal to (=)" sign. In terms of gram equivalents (geq), we have :

$$\text{geq of } A_1 = \text{geq of } A_2 = \text{geq of } A_3 = \text{geq of } A_4$$

$$N_1V_1 = N_2V_2 = N_3V_3 = N_4V_4$$

Consideration in normality gives a relation that are connected with "equal to (=)" sign. It is so because constituents react in the proportion of equivalent weights. As such, gram equivalents are equal. Clearly, analysis involving normality is relatively easier to handle.

Example:

Problem : A 25 ml of nitric acid taken from a stock volume of 1 litre neutralizes 50 ml of 0.1N NaOH solution. Determine the mass of nitric acid in the stock volume.

Solution : Let us denote nitric acid and sodium hydroxide by subscripts "1" and "2" respectively. Applying neutralization equation,

$$\begin{aligned} N_1V_1 &= N_2V_2 \\ \Rightarrow N_1 \times 25 &= 0.1 \times 50 \\ \Rightarrow N_1 &= \frac{5}{25} = 0.2 \end{aligned}$$

The normality of sample and the stock volume is same. Hence, normality of 1 litre stock volume is 0.2N. Using formula,

$$\Rightarrow \text{geq} = NV = 0.2 \times 1 = 0.2 = \frac{g_B}{E} = \frac{x g_B}{M_O}$$

Valence factor of nitric acid is 1 as it has one furnishable hydrogen. Therefore,

$$\Rightarrow g_B = \frac{0.2 M_O}{x} = \frac{0.2 \times (1 + 14 + 3 \times 16)}{1} = 12.6 \text{ gm}$$

Successive neutralization

In this case, data of two or more neutralization reactions is analyzed to determine unknown concentration of solution.

Example:

Problem : 18 ml of 0.1N H_2SO_4 is neutralized by 20 ml of a NaOH solution. On the other hand, 10 ml of oxalic acid is required to neutralize the same volume of NaOH solution. Determine the mass of oxalic acid crystals $\{(COOH)_2 \cdot 2H_2O\}$ used.

Solution : A solution of known concentration of sulphuric acid neutralizes sodium hydroxide solution of unknown concentration. Applying neutralization equation, we determine normality of sodium hydroxide solution :

$$\begin{aligned} N_1V_1 &= N_2V_2 \\ \Rightarrow 0.1 \times 18 &= N_2 \times 20 \\ \Rightarrow N_2 &= \frac{1.8}{20} = 0.09N \end{aligned}$$

Now, a solution of known concentration of sodium hydroxide neutralizes oxalic acid solution of unknown concentration. Again applying neutralization equation, we determine normality of oxalic acid solution :

$$\begin{aligned} N_1V_1 &= N_2V_2 \\ \Rightarrow 0.09 \times 20 &= N_2 \times 10 \\ \Rightarrow N_2 &= \frac{1.8}{10} = 0.18N \end{aligned}$$

Using formula,

$$\Rightarrow \text{geq} = NV = \frac{0.19 \times 10}{1000} = \frac{1.9}{1000} = 0.0019 = \frac{g_B}{E} = \frac{xg_B}{M_O}$$

Valence factor of oxalic acid is 2 as it has two furnishable hydrogens. Therefore,

$$\Rightarrow g_B = \frac{0.0019M_O}{x} = \frac{0.0019 \times \{2 \times (12 + 2 \times 16 + 1) + 2 \times 18\}}{2} = 0.1197 \text{ gm}$$

Dilution and neutralization

The resulting solution of two or more solutions or diluted solution is neutralized by other solution.

Example:

Problem : 5 ml each of 2N hydrochloric and 3N nitric acids volumes are mixed with a certain volume of 5N sulphuric and the resulting solution is made up to 1 litre. A volume of 25 ml of this solution neutralizes 50 ml of sodium carbonate solution containing 1 gm of $Na_2CO_3 \cdot 10H_2O$ in water. Determine the volume of sulphuric acid in the mixture.

Solution : A combination of different acids are used here. The mixture is then diluted up to 1 litre. Let the volume of sulphuric acid used is x ml. Here, milli-gram equivalents of the mixture is :

$$\Rightarrow \text{meq} = 5 \times 2 + 5 \times 3 + 5x = 25 + 5x$$

Applying equation of dilution,

$$\begin{aligned} N_1V_1 &= N_2V_2 \\ \Rightarrow 25 + 5x &= N_2 \times 1000 \end{aligned}$$

$$\Rightarrow N_2 = \frac{25 + 5x}{1000}$$

We see here that normality of acid solution has one unknown. 25 ml of diluted acid neutralizes 50 ml of sodium carbonate solution. Clearly, we need to calculate normality of sodium carbonate used. We see here that strength of sodium carbonate solution is given (1 gm/50 ml = 20 gm/l). Using relation,

$$S = NE$$

The valence factor of sodium carbonate is 2 as its cation or anion has 2 electronic charge.

$$\Rightarrow N = \frac{S}{E} = \frac{xS}{M_O} = \frac{2 \times 20}{(2 \times 23 + 12 + 3 \times 16 + 10 \times 18)} = \frac{40}{286} = 0.14N$$

Now, using neutralization equation :

$$N_1V_1 = N_2V_2$$

$$\Rightarrow \frac{25 + 5x}{1000} \times 25 = 0.14 \times 50$$

$$\Rightarrow 25 + 5x = 0.28 \times 1000 = 280$$

$$\Rightarrow 5x = 280 - 25 = 255$$

$$\Rightarrow x = \frac{255}{5} = 51 \text{ ml}$$

Neutralization of oleum

Oleum is concentrated sulphuric acid and free sulphur trioxide (SO_3). When SO_3 reacts with water, it produces sulphuric acid.



It means that SO_3 molecule is equivalent to sulphuric acid in the presence of water. Thus, neutralization of base with oleum acid will follow the equivalence as :

$$\text{geq of } H_2SO_4 + \text{geq of } SO_3 = \text{geq of base}$$

Example:

Problem : 1 gm of oleum is diluted in water. The resulting solution requires 45 ml of 0.5N sodium hydroxide solution for neutralization. Determine the mass of free SO_3 in the oleum.

Solution : Let mass of SO_3 in oleum is x . Then, mass of sulphuric acid in the oleum is $1-x$. We can find gram-equivalents of the sulphuric acid and oleum provided we know valence factors. The valence factor of each of them is 2. Hence, equivalent weights of sulphuric acid and Sulphur trioxide are $98/2=49$ and $80/2=40$ respectively. Applying neutralization equation,

$$\text{geq of } H_2SO_4 + \text{geq of } SO_3 = \text{geq of base}$$

$$\frac{1-x}{49} + \frac{x}{40} = NV = \frac{0.5 \times 45}{1000} = \frac{22.5}{1000}$$

$$\Rightarrow 40 - 40x + 49x = 49 \times 40 \times \frac{22.5}{1000} = 44.100$$

$$\Rightarrow 9x = 4.41$$

$$\Rightarrow x = \frac{4.41}{9} = 0.5 \text{ gm}$$

Titration

Titration is an analytical laboratory method to determine concentration of a solution. It is based on volumetric stoichiometric analysis involving two or more solutions. In most of the cases, we shall refer aqueous solutions. Clearly, titration is limited to substances, which are soluble in some solvent (may be at a higher temperature). Further, scope of titration is wider than acid-base neutralization reactions. The redox reactions and other complex forming reactions are also studied using titration.

Completion of reaction (equivalence point) is determined using some technique that includes chemical indicators, potentiometer, pH meter and many other techniques. Sometimes, even the change in the color of reacting solution signals the end of titration. In the case of acid base reaction, chemical indicators like methyl orange or phenolphthalein are used to determine end point. These indicators changes color with the change in the pH of the solution.

Some important terms or descriptions used in titration are :

Titrant : It is the standard solution whose concentration is known. It is placed in a thin cylindrical pipe called burette with fine measuring divisions to determine volume accurately. The titrant is streamed drop by drop into the flask containing reactant/ analyte.

Reactant/ analyte : It is the solution whose concentration is not known. Titration method is used to analyze this solution. An accurate volume of the reactant is kept in conical flask. The pH measuring techniques or devices are associated with reactant volume. If chemical indicator is used to identify end point, then very small amount of indicator (few drops) is mixed with the reactant.

Acid base titration indicators

Acid base titration makes use of pH chemical indicators, which changes color in a band of pH values – not at a particular pH value. Typically, we use methyl orange and phenolphthalein to determine end points of acid-base titration. The selection of a particular indicator for the titration is decided on the basis of plot known as pH curve, which is typical of a particular reaction. The indicator is always added to the reactant in the flask.

Methyl orange

Methyl orange is a weak base. It gives end points between pH range between 3.1 and 4.4. In weak acidic or basic environment ($\text{pH} > 4.4$), its color is yellow. In high acidic environment ($\text{pH} < 3.1$), it is red in color. In the detection range ($\text{pH} : 3.1 \text{ to } 4.4$), its color is orange. The color changes from yellow to orange (when solution pH falls towards detection range) or red to orange (when solution pH rises towards detection range), indicating equivalence point.

Phenolphthalein

Phenolphthalein is a weak acid. It gives end points between pH range between 8.3 and 10. In strong acidic and weak basic environment ($\text{pH} < 8.3$), it is colorless. In strong basic environment ($\text{pH} > 10$), it is pink in color. In the detection range ($\text{pH} : 8.8 \text{ to } 10$), its color is pale pink. The color changes from colorless to pale pink (when solution pH rises towards detection range) or from pink to pale pink (when solution pH falls towards detection range), indicating equivalence point.

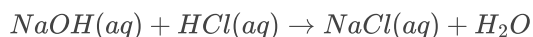
pH plots

The pH values are plotted against the volume of titrant (acid or base). Except for weak acid – weak base, there is a sharp change in pH value at the equivalence point. The plot is almost parallel to pH axis. The sharp range at equivalence point is due to the fact that pH itself is a logarithm function of hydrogen ion concentration. The

gradual change away from equivalence point is explained on the basis of buffering effect of acid or base as the case be.

Strong acid – strong base

The reaction considered here is :

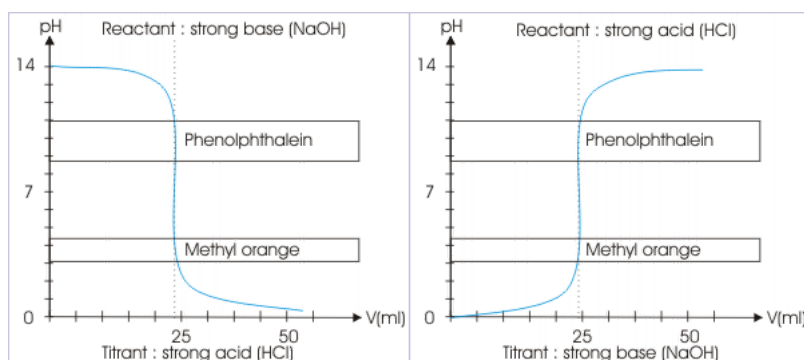


In the pH plot in which acid is titrant, pH of the solution in the flask is 14 due to strong base (NaOH). As strong acid is added, pH is almost flat till the equivalence point volume, when there is sharp drop in pH value. The extent of drop or rise depends on the reaction rate, which is very fast for strong acid- strong base reaction. The pH drop at equivalence point can induce color change in either of two indicators as drop in pH covers color change range for two indicators.

pH plots

Acid is titrant.

Base is titrant



In the pH plot in which base is titrant, pH of the solution in the flask is near zero due to strong acid (HCl). As strong base is added, pH is almost flat in the beginning till the equivalence point volume, when there is sharp rise in pH value. The pH increase at equivalence point can induce color change in either of two indicators as rise in pH covers color change range for two indicators.

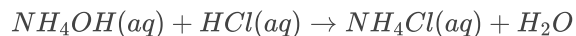
volume of HCl used = volume acid required for neutralization of NaOH

This means that :

geq of HCl = geq of NaOH (indicator : methyl orange or phenolphthalein)

Strong acid – weak base

The reaction considered here is :

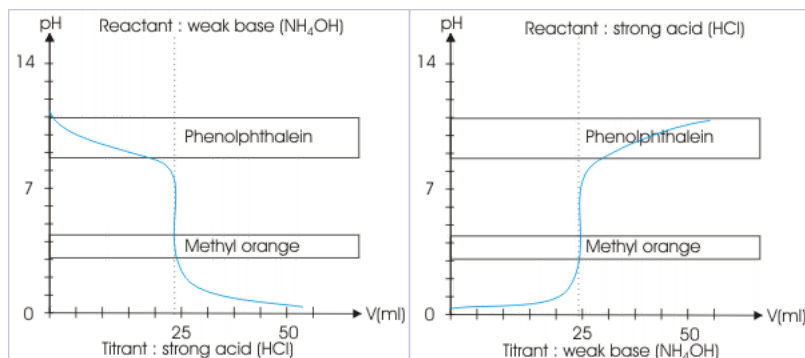


In the pH plot in which acid is titrant, pH of the solution in the flask is about 11 due to weak base (NH_4OH). As strong acid (HCl) is added, pH drops gently till the equivalence point volume. The extent of drop in pH is lesser in comparison to strong acid - strong base reaction as reaction rate is relatively slower. The pH drop at equivalence point is shorter and can induce color change in methyl orange only.

pH plots

Acid is titrant.

Base is titrant



In the pH plot in which base is titrant, pH of the solution in the flask is near zero due to strong acid (HCl). As weak base is added, pH is almost flat in the beginning till the equivalence point volume, when there is sharp rise in pH value. The pH rise at equivalence point is shorter and can induce color change in methyl orange only.

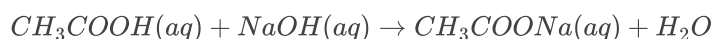
volume of HCl used = volume acid required for neutralization of NH_4OH

This means that :

geq of HCl = geq of NH_4OH (indicator : methyl orange)

Weak acid – strong base

The reaction considered here is :

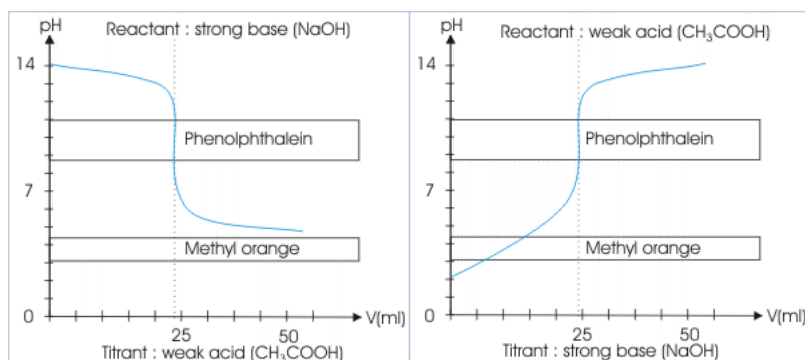


In the pH plot in which acid is titrant, pH of the solution in the flask is about 14 due to strong base (NaOH). As weak acid (HCl) is added, pH drops gently till the equivalence point volume. The extent of drop in pH is lesser in comparison to strong acid - strong base reaction as reaction rate is relatively slower. The pH drop at equivalence point is shorter and can induce color change in phenolphthalein only.

pH plots

Acid is titrant.

Base is titrant



In the pH plot in which base is titrant, pH of the solution in the flask is near 2-3 due to weak acid (CH_3COOH). As strong base is added, pH rises in the beginning till the equivalence point volume, when there is sharp rise in

pH value. The pH rise at equivalence point is shorter and can induce color change in phenolphthalein only.

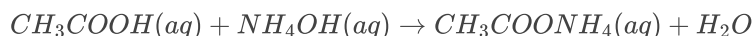
volume of CH_3COOH used = volume acid required for neutralization of NaOH

This means that :

geq of CH_3COOH = geq of NaOH (indicator : phenolphthalein)

Weak acid – weak base

The reaction considered here is :



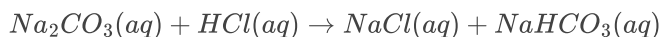
There is no sharp change in pH value at equivalence point. The pH value is approximately 7 at equivalence. In this case, there is only a point of inflexion (against extended vertical shift in pH value as observed in earlier cases), which can be detected with confidence.

Two stage titration

Few reactions are completed in two stages. Corresponding to each stage, there is an equivalence point. We need to employ suitable indicator to identify completion of individual reaction. We decide selection of the indicator based on the range of pH change at equivalence volume of the titrant.

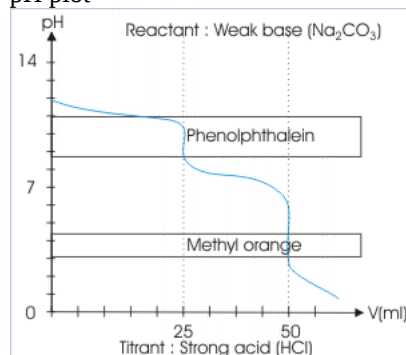
Sodium carbonate and hydrochloric acid

The reaction is completed in two stages. The first stage reaction is :



Considering that HCl is the titrant, we see that sodium bicarbonate is intermediate product, which is itself a basic salt. It means that pH value remains in basic range above 7. The equivalence volume of acid corresponds to formation of sodium bicarbonate. Clearly, phenolphthalein can detect the drop of pH value at equivalence. However, this detection will not correspond to complete titration of sodium carbonate as sodium bicarbonate is further acted on by the acid according to the second stage reaction as given here :

pH plot



Acid is titrant.



The important aspect of this reaction is that carbon dioxide is acidic and as such pH of the solution further goes down. On the completion of reaction, there is sharp drop in pH value which falls within the range of color change of methyl orange. Thus, methyl orange detects the completion of reaction of sodium carbonate with hydrochloric acid.

$$\text{geq of HCl} = \text{geq of } Na_2CO_3 \quad (\text{indicator : methyl orange})$$

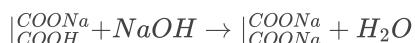
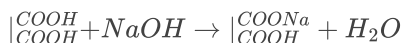
It is clear from the description that phenolphthalein can not detect completion of reaction of acid with sodium carbonate. There is, however, an interesting aspect about the equivalence volumes involved in two stages of reaction. The first equivalence volume (25 ml) is exactly half of the second equivalence volume (50 ml). We can conclude that first equivalence volume with phenolphthalein gives exactly half of the reaction with sodium carbonate.

$$\text{geq of HCl} = \frac{1}{2} \text{geq of } Na_2CO_3 \quad (\text{indicator : methyl orange})$$

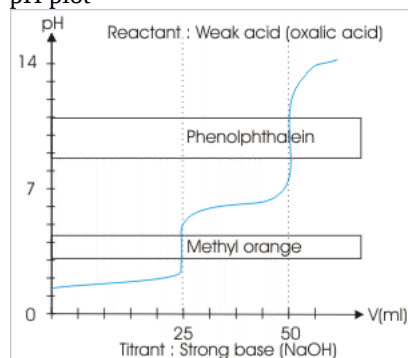
This is how phenolphthalein can also be used to estimate sodium carbonate concentration – even though it does not detect completion of the reaction. It should also be emphasized that neutralization of sodium bicarbonate is detected by methyl orange - not by phenolphthalein. We may conclude that phenolphthalein can not detect neutralization of sodium bicarbonate.

Oxalic acid sodium hydroxide

The reaction involved here is also completed in two stages. Oxalic acid has two furnishable hydrogen ions. Two hydrogen ions are replaced one after other in two stages :



pH plot



Base is titrant.

Considering that sodium hydroxide is titrant, we see that one of two hydrogens of oxalic acid is replaced by sodium in the first stage. It can be seen that methyl orange can detect the rise of pH value at equivalence at the end of first stage reaction. On the other hand, completion of second stage reaction is detected by phenolphthalein. Following earlier logic, we conclude :

$$\text{geq of NaOH} = \text{geq of oxalic acid} \quad (\text{indicator : phenolphthalein})$$

$$\text{geq of NaOH} = \frac{1}{2} X \text{geq of oxalic acid (indicator : methyl orange)}$$

Titration of basic mixtures

We can titrate mixtures of basic compounds with strong acid like HCl. Consider the combination of bases :

1: NaOH and Na_2CO_3

2: NaHCO_3 and Na_2CO_3

Mixture of sodium hydroxide and sodium carbonate

The analysis depends on the particular indicator used. If we use methyl orange, then we know that it can detect completion of reaction of HCl with either of two basic compounds. Hence,

$$\text{volume of HCl used} = \text{volume acid required for neutralization of NaOH and } \text{Na}_2\text{CO}_3$$

This means that :

$$\text{geq of HCl} = \text{geq of NaOH} + \text{geq of } \text{Na}_2\text{CO}_3 \text{ (indicator : methyl orange)}$$

If we use phenolphthalein, then we know that it can detect completion of reaction of HCl with NaOH. However, it can detect only half of the completion of reaction of HCl with sodium carbonate.

$$\text{volume of HCl used} = \text{volume acid required for neutralization of NaOH} + \frac{1}{2} \text{volume acid required for ne}$$

This means that :

$$\text{geq of HCl} = \text{geq of NaOH} + \frac{1}{2} X \text{geq of } \text{Na}_2\text{CO}_3 \text{ (indicator : phenolphthalein)}$$

Q. A volume of 25 ml of 0.2 N HCl is titrated to completely neutralize 25 ml mixture of NaOH and Na_2CO_3 , using phenolphthalein as indicator. On the other hand, 60 ml of 0.1 N HCl is required to neutralize the equal volume of mixture, using methyl orange as indicator. Find the strengths of NaOH and Na_2CO_3 in the mixture.

Answer : Strength is expressed in terms of gm/litre. Thus, we need to know the mass of each component in the mixture. First titration uses phenolphthalein, which detects completion of reaction with NaOH and half of reaction with Na_2CO_3 . Hence,

$$\text{meq of acid} = \text{meq of NaOH} + \frac{1}{2} X \text{meq of } \text{Na}_2\text{CO}_3$$

Clearly, it is helpful to assume unknowns in terms of milli-equivalents (meq) instead of mass. Once, meq are calculated, we convert the same finally in mass terms and strength of solution as required. Let x and y be the meq of NaOH and Na_2CO_3 in the mixture.

Putting values in the equation, we have :

$$\Rightarrow N_a V_a = x + 0.5y$$

$$\Rightarrow x + 0.5y = 0.2 \times 25 = 5$$

Second titration uses methyl orange, which detects completion of reaction with both NaOH and Na_2CO_3 . Hence,

$$\text{meq of acid} = \text{meq of NaOH} + \text{meq of } \text{Na}_2\text{CO}_3$$

$$\Rightarrow N_a V_a = x + y$$

$$\Rightarrow x + y = 0.1 \times 60 = 6$$

Solving two equations (subtracting first from second equation), we have

$$\Rightarrow 0.5y = 1$$

$$\Rightarrow y = 2$$

and

$$\Rightarrow x = 6 - 2 = 4$$

Now, we need to convert meq into strength of solution. For that, we first convert meq to mass of solute (B) in gram.

$$\text{meq} = \text{valence factor} \times \text{milli-moles}$$

$$\Rightarrow \text{meq} = \frac{\text{valence factor} \times g_B \times 1000}{M_B}$$

$$\Rightarrow g_B = \frac{M_B \times \text{meq}}{\text{valence factor} \times 1000}$$

Thus, strength of component in 25 ml solution is :

$$\Rightarrow S = \frac{g_B \times 1000}{25} = \frac{M_B \times \text{meq} \times 1000}{25 \times \text{valence factor} \times 1000} = \frac{M_B \times \text{meq}}{25 \times \text{valence factor}}$$

Putting values, strength of NaOH is :

$$\Rightarrow S = \frac{M_B \times \text{meq}}{25 \times \text{valence factor}} = \frac{40 \times 4}{25 \times 1} = 6.4 \text{ gm/l}$$

Similarly, strength of Na_2CO_3 is :

$$\Rightarrow S = \frac{M_B \times \text{meq}}{25 \times \text{valence factor}} = \frac{106 \times 4}{25 \times 2} = 4.24 \text{ gm/l}$$

Mixture of sodium bicarbonate and sodium carbonate

The analysis again depends on the particular indicator used. If we use methyl orange, then we know that it can detect completion of reaction of HCl with either of two basic compounds. Hence,

$$\text{volume of HCl used} = \text{volume acid required for neutralization of } \text{NaHCO}_3 \text{ and } \text{Na}_2\text{CO}_3$$

This means that :

$$\text{geq of HCl} = \text{geq of } \text{NaHCO}_3 + \text{geq of } \text{Na}_2\text{CO}_3 (\text{indicator : methylorange})$$

If we use phenolphthalein, then we know that it can detect one half of completion of reaction of HCl with Na_2CO_3 . However, it can not detect completion of reaction of HCl with NaHCO_3 .

$$\text{volume of HCl used} = \frac{1}{2} \times \text{volume of acid required for neutralization of } \text{Na}_2\text{CO}_3$$

This means that :

$$\text{geq of HCl} = \frac{1}{2} X \text{geq of } Na_2CO_3 (\text{indicator : phenolphthalein})$$

Q. A volume of 40 ml of 0.1 N HCl is titrated to completely neutralize 25 ml of basic solution containing Na_2CO_3 and $NaHCO_3$, using methyl orange as indicator. On the other hand, 15 ml of 0.1 N HCl is required to neutralize equal volume of basic solution, using phenolphthalein as indicator. Find the strength of Na_2CO_3 and $NaHCO_3$ in the solution.

Answer : First titration uses methyl orange, which detects completion of reaction with both Na_2CO_3 and $NaHCO_3$. Hence,

$$\text{meq of acid} = \text{meq of } Na_2CO_3 + \text{meq of } NaHCO_3$$

Let x and y be the meq of Na_2CO_3 and $NaHCO_3$ in the mixture. Putting values in the equation, we have :

$$\Rightarrow N_a V_a = x + y$$

$$\Rightarrow x + y = 0.1 \times 40 = 4$$

Second titration uses phenolphthalein, which detects completion of half reaction with Na_2CO_3 . It does not detect completion of reaction with respect to $NaHCO_3$. Hence,

$$\text{meq of acid} = \frac{1}{2} X \text{meq of } Na_2CO_3$$

$$\Rightarrow N_a V_a = \frac{1}{2} x$$

$$\Rightarrow \frac{1}{2} x = 0.1 \times 15 = 1.5$$

$$\Rightarrow x = 3$$

Putting in the first equation, we have

$$\Rightarrow y = 4 - 3 = 1$$

Now, we need to convert meq into strength of solution. Using formula as derived earlier,

$$\Rightarrow S = \frac{M_B X \text{meq}}{V_{CC} X \text{valence factor}}$$

Putting values, strength of Na_2CO_3 is :

$$\Rightarrow S = \frac{M_B X \text{meq}}{V_{CC} X \text{valence factor}} = \frac{106 \times 3}{25 \times 2} = 6.36 \text{ gm/l}$$

Similarly, strength of $NaHCO_3$ is :

$$\Rightarrow S = \frac{M_B X \text{meq}}{V_{CC} X \text{valence factor}} = \frac{84 \times 1}{25 \times 1} = 3.36 \text{ gm/l}$$

Back titration

Back titration is also titration. It is called back titration because it is not carried out with the solution whose concentration is required to be known (analyte) as in the case of normal or forward titration, but with the excess volume of reactant which has been left over after completing reaction with the analyte. Back titration works in the following manner (with an example) :

1: The substance or solution of unknown concentration (4 gm of contaminated chalk, $CaCO_3$) is made to react with known volume and concentration of intermediate reactant solution (200 ml, 0.5N HCl). The reaction goes past the equivalence point. The amount of intermediate reactant is in excess of that required for completing reaction with analyte.

2: After completing the reaction with analyte, the resulting solution containing excess of intermediate reactant is titrated with known volume and concentration of titrant (50 ml of 0.5N NaOH). If subscripts 1 and 2 denotes intermediate reactant and titrant, then

$$\begin{aligned}N_1V_1 &= N_2V_2 \\ \Rightarrow 0.5V &= 0.5 \times 50 \\ \Rightarrow \text{volume of excess HCl, } V &= 50 \text{ ml}\end{aligned}$$

Also,

$$\text{meq of excess HCl} = \text{meq of titrant, NaOH} = 0.5 \times 50 = 25$$

3: Determination of excess volume or meq of intermediate reactant allows us to determine the volume or meq of intermediate reactant which reacted with analyte. This, in turn, lets us determine the amount of analyte.

$$\begin{aligned}\Rightarrow \text{meq of chalk} &= \text{total meq of HCl} - \text{meq of excess HCl} \\ \Rightarrow \text{meq of chalk} &= 0.5 \times 200 - 25 \\ \Rightarrow \text{meq of chalk} &= \text{meq of HCl used for chalk} = 75\end{aligned}$$

Applying gram equivalent concept to chalk and HCl,

$$\Rightarrow \text{meq of chalk} = \text{meq of HCl used for chalk} = 75$$

$$\frac{g}{E} \times 1000 = \frac{2 \times 1000g}{(40 + 12 + 3 \times 16)} = 75$$

$$\Rightarrow g = \frac{75}{20} = \frac{15}{4} = 3.75 \text{ gm}$$

This means chalk contained 0.25 gm of impurities in it.

Purpose of back titration

Back titration is designed to resolve some of the problems encountered with forward or direct titration. Possible reasons for devising back titration technique are :

1: The analyte may be in solid form like chalk in the example given above.

2: The analyte may contain impurities which may interfere with direct titration. Consider the case of contaminated chalk. We can filter out the impurities before the excess reactant is titrated and thus avoid this situation.

3: The analyte reacts slowly with titrant in direct or forward titration. The reaction with the intermediate reactant can be speeded up and reaction can be completed say by heating.

4: Weak acid – weak base reactions can be subjected to back titration for analysis of solution of unknown concentration. Recall that weak acid-weak base titration does not yield a well defined change in pH, which can be detected using an indicator.

Example:

Problem : 50 litres of air at STP is slowly bubbled through 100 ml of 0.03N $Ba(OH)_2$ solution. The $BaCO_3$ formed due to reaction is filtered and few drops of Phenolphthalein is added to the solution rendering it pink. The solution required 25 ml of 0.1 N HCl solution when indicator turned colorless. Calculate percentage by volume of CO_2 in air.

Solution : Carbon dioxide reacts with $Ba(OH)_2$ to form $BaCO_3$. The excess $Ba(OH)_2$ is back titrated with HCl.

$$\text{total meq of } Ba(OH)_2 \text{ solution} = 0.03 \times 100 = 3$$

$$\text{meq of excess } Ba(OH)_2 \text{ solution} = 0.1 \times 25 = 2.5$$

$$\text{meq of } Ba(OH)_2 \text{ solution used for } CO_2 = 3 - 2.5 = 0.5$$

$$g = \frac{\text{meq} \times M_O}{1000} = \frac{0.5 \times (12 + 2 \times 16)}{1000 \times 2} = 0.01 \text{ gm}$$

Using Avogadro's hypothesis, 44 gm of CO_2 occupies 22.4 litres at STP. This mass of CO_2 corresponds to :

$$\text{volume of } CO_2 = \frac{22.4 \times 0.01}{44} = 0.01 \text{ litres}$$

$$\Rightarrow \% \text{ of } CO_2 \text{ in air} = \frac{0.01 \times 100}{50} = 0.02$$

Back titration and dilution

While dealing dilution in titration calculation, we need only to remember that dilution does not change meq or meq of a solution.

Example:

Problem : 2.75 gram of a sample of dolomite containing $CaCO_3$ and $MgCO_3$ is dissolved in 80 ml 1N HCl solution. The solution is then diluted to 250 ml. 25 ml of this solution requires 20 ml of 0.1 N NaOH solution for complete neutralization. Calculate percentage composition of the sample.

Solution : We shall first determine the amount of HCl required to react with the sample by using back titration data. Here, we make use the fact that dilution does not change meq of a solution.

$$\Rightarrow \text{meq of 25 ml of diluted excess HCl solution} = \text{meq of NaOH solution} = 0.1 \times 20 = 2$$

$$\Rightarrow \text{meq of 250 ml of diluted excess HCl solution} = 20$$

$$\Rightarrow \text{total meq of HCl} = NV = 80 \times 1 = 80$$

$$\text{meq of HCl used to react with dolomite} = 80 - 20 = 60$$

Mass of HCl used in reaction with dolomite is calculated using expression of meq :

$$meq = \frac{g}{E} \times 1000 = \frac{xg}{M_O} \times 1000$$

$$\Rightarrow g = \frac{meq \times M_O}{1000x} = \frac{60 \times 36.5}{1000 \times 1} = 2.19 \text{ gm}$$

In order to find the composition, we apply mole concept. The reactions involved are :



Let mass of $CaCO_3$ in the sample is x gm. Then mass of $MgCO_3$ is 2.75-x gm.

$$\frac{x}{M_{CaCO_3}} \text{ moles of } CaCO_3 = \frac{x}{100} \text{ moles of } CaCO_3 = \frac{2x}{100} \text{ moles of HCl}$$

$$\Rightarrow \text{mass of HCl required for } CaCO_3 = \frac{2x \times M_{HCl}}{100} = \frac{2x \times 36.5}{100} = \frac{73x}{100} = 0.73x \text{ gm}$$

Similarly for $MgCO_3$,

$$\Rightarrow \text{mass of HCl required for } MgCO_3 = \frac{2(2.75 - x)M_{HCl}}{84} = \frac{2 \times (2.75 - x) \times 36.5}{84} = \frac{73(2.75 - x)}{84} = 2.39$$

$$\Rightarrow \text{total HCl required} = 0.73x + 2.39 - 0.87x = 2.19$$

$$\Rightarrow 0.14x = 0.2$$

$$x = 1.43 \text{ gm}$$

$$\Rightarrow \% \text{ mass of } CaCO_3 = \frac{1.43}{2.75} \times 100 = 52$$

$$\Rightarrow \% \text{ mass of } MgCO_3 = 100 - 52 = 48$$

Back titration and decomposition

Back titration is analyzed using geq or meq concept. On the other hand, decomposition is analyzed using mole concept. We combine two concepts by converting final geq or meq data of back titration into either mass or moles.

Example:

Problem : 4.08 gm of a mixture of BaO and an unknown carbonate MCO_3 is heated strongly. The residue weighs 3.64 gram. The residue is then dissolved in 100 ml of 1 N HCl. The excess acid requires 16 ml of 2.5 NaOH for complete neutralization. Identify the metal M, if atomic weight of Ba is 138.

Solution : We need to determine atomic weight of M to identify it. From the question, we see that first part involves decomposition, which can be analyzed using mole concept. Note that difference of mass of mixture and residue is mass of CO_2 . On the other hand, analysis of back titration gives us meq of HCl required for neutralization of residue. To combine meq data with decomposition data, we shall convert required meq in millimoles.

$$\Rightarrow \text{total meq of HCl} = NV = 1 \times 100 = 100$$

$$\Rightarrow \text{meq of excess HCl} = NV = 2.5 \times 16 = 40$$

$$\Rightarrow \text{meq of HCl used for neutralization of residue} = 100 - 40 = 60$$

$$\Rightarrow \text{milli-moles of HCl for neutralization of residue} = xX\text{meq} = 1X60 = 60$$

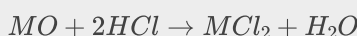
Now, we analyze the data which is given for decomposition of mixture. On heating, BaO is not decomposed. Only MCO_3 is decomposed as :



Carbon dioxide is released and is not part of residue. The amount of CO_2 is equal to difference of mass of mixture and residue. Hence, moles of CO_2 released are :

$$\Rightarrow n_{CO_2} = \frac{4.08 - 3.64}{(12 + 2X16)} = \frac{0.44}{44} = 0.01 \text{ mole}$$

Applying mole concept, moles of MO in the residue is 0.01 mole i.e. 10 milli-moles. Now, MO reacts with HCl as :



Moles of HCl required for MO is $2X0.01$ moles = 20 milli-moles of HCl. But total milli-moles that reacted with residue is 60 milli-moles. Hence, milli-moles of HCl that reacted with BaO is $60 - 20 = 40$ milli-moles of HCl. Applying mole concept,



The milli-moles of BaO is half of that of HCl. Hence, millimoles of BaO in the mixture is 20 milli-moles.

$$\Rightarrow \text{amount of BaO in the mixture} = \frac{\text{milli-moles} \times M_{BaO}}{1000} = \frac{20X(138 + 16)}{1000} = 3.08 \text{ gm}$$

$$\Rightarrow \text{amount of MO in the residue} = 3.64 - 3.08 = 0.56 \text{ gm}$$

Using formula :

$$\Rightarrow g = \frac{\text{milli-moles} \times M_{MO}}{1000} = \frac{10X M_{MO}}{1000}$$

$$\Rightarrow M_{MO} = 100g = 100X0.56 = 56$$

Clearly, atomic weight of M is $56 - 16 = 40$. The element, therefore, is calcium.

Back titration and multiple neutralizations

The concentration of titrant used to determine the excess reactant is not directly given. We make use of subsequent neutralization data to ultimately determine the concentration of titrant.

Example:

Problem : A sample of $MnSO_4 \cdot 4H_2O$ (molecular wt : 223) is heated in air. The residue is Mn_3O_4 , whose valency and molecular weight are 2 and 229 respectively. The residue is dissolved in 100 ml of 0.1 N $FeSO_4$ solution containing dilute sulphuric acid. The resulting solution reacts completely with 50 ml of $KMnO_4$ solution. 25 ml of the $KMnO_4$ solution requires 30 ml of 0.1N $FeSO_4$ solution for complete oxidation. Calculate the weight of $MnSO_4 \cdot 4H_2O$ in the given sample.

Solution : The excess of $FeSO_4$ completely reacts with 50 ml of $KMnO_4$ solution of unknown concentration. We need to know this concentration. From the data of complete oxidation, however, we can know concentration.

Let 1 and 2 subscripts denote $KMnO_4$ and $FeSO_4$, then

$$\begin{aligned} N_1 V_1 &= N_2 V_2 \\ \Rightarrow N_1 \times 25 &= 0.1 \times 30 \\ \Rightarrow N_1 &= \frac{3}{25} = 0.12N \end{aligned}$$

Now, considering back titration,

$$\begin{aligned} \Rightarrow \text{total meq of } FeSO_4 \text{ solution} &= 0.1 \times 100 = 10 \\ \Rightarrow \text{meq of excess } FeSO_4 \text{ solution} &= 0.12 \times 50 = 6 \\ \Rightarrow \text{meq of } FeSO_4 \text{ solution used for residue} &= 10 - 6 = 4 \\ \Rightarrow \text{meq of } Mn_2O_3 \text{ in the residue} &= 4 \end{aligned}$$

Mass of Mn_2O_3 is determined using meq expression :

$$\begin{aligned} meq &= \frac{g}{E} \times 1000 = \frac{xg}{M_O} \times 1000 \\ \Rightarrow g &= \frac{meq \times M_O}{1000} = \frac{4 \times 229}{1000} = 0.916 \text{ gm} \end{aligned}$$

The decomposition of $MnSO_4 \cdot 4H_2O$ takes place as :



Applying mole concept, the amount of $MnSO_4 \cdot 4H_2O$ is :

$$\Rightarrow \text{Mass of } MnSO_4 \cdot 4H_2O = \frac{3 \times 229}{229} \times 0.916 = 2.748 \text{ gm}$$